finishing

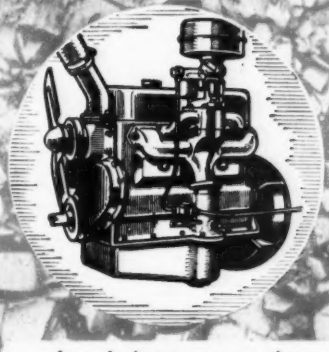
Vol. 2 No. 17 (new series) MAY, 1956

PHOSPHATE PROCESSES

approved for every purpose . . .*

for bonding paint to metal surfaces . .

for resisting corrosion . . .



for reducing wear on moving (ferrous) parts . . .

for facilitating the cold working of steel . . .

BONDERIZING · PARKERIZING · PARCO-LUBRIZING

group of Pyrene Metal Finishing Processes

THE PYRENE COMPANY LTD. · METAL FINISHING DIVISION

GREAT WEST ROAD · BRENTFORD · MIDDLESEX *Telephone:* EALing 5444

GALVATITE

metal finishing Journal

MAY, 1956 — AN INDUSTRIAL NEWSPAPERS PUBLICATION — Vol. 2 No. 16 (New Series)

Editor: JOHN HOOPER *Managing Editor:* ALASTAIR MCLEOD, F.I.M. *Assistant Editor:* E. H. LLOYD, A.I.M., A.C.T.(Birm.)
Southern Area Manager: E. COLLIS *Northern Area Manager:* G. P. ELLIOTT *Scottish Area Manager:* T. H. SMITH
Western Area Manager: E. J. SWEETING *Eastern Area Manager:* ERIC PERRIN
Production Manager: R. J. LOVELL *Circulation Manager:* E. T. GRIFFITHS *Publisher:* H. J. DWYER

Official Organ of the

INSTITUTE OF VITREOUS ENAMELLERS

President:
SIR GEORGE BRIGGS

Chairman:
H. LAITHWAITE

Secretary:
J. D. GARDOM
John Gardom & Co., Ripley, Derby
Telephone: Ripley 136

Published on the 15th of each month by

INDUSTRIAL NEWSPAPERS LIMITED

Chairman and Managing Director:
Barrington Hooper, C.B.E.
Commercial Director:
F. Barrington Hooper, B.A.
Director:
F. R. Lewis
Director and Secretary:
E. G. Weston

JOHN ADAM HOUSE
17-19 JOHN ADAM STREET
ADELPHI, LONDON, W.C.2
Telephone: TRAfalgar 6171 (P.B.X.)
Telegrams: Zacatecas, Rand, London

Subscription Terms:
Home and Overseas 24*s.* per annum prepayable
Single copies 2*s.* (2*s.* 4*d.* *post free*)

THIS JOURNAL IS DEVOTED TO THE SCIENCE AND TECHNOLOGY OF PAINT APPLICATION, ELECTRODEPOSITION, VITREOUS ENAMELLING, GALVANIZING, ANODIZING, METAL SPRAYING AND ALL METAL FINISHING PROCESSES.

THE EDITOR IS PREPARED TO CONSIDER FOR PUBLICATION ANY ARTICLE COMING WITHIN THE PURVIEW OF METAL FINISHING JOURNAL AND ALL SUCH ARTICLES ACCEPTED WILL BE PAID FOR AT THE USUAL RATES.

Contents

page

Signs of the Times 123

Talking Points 124
" Platelayer "

METAL FINISHING ANNUAL CONFERENCE 125

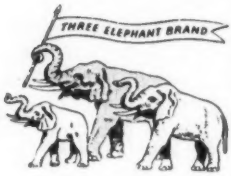
Solution Ceramics 145
T. A. Dickinson

An Investigation into the Viscosity of Enamels 151
N. S. C. Millar, A.R.I.C., and C. H. Bucke, B.Sc.(Hon.)

The Work of the Corrosion Section at Fulmer Research Institute 157

News Review 161

Plant, Processes and Equipment 167



B_2O_3

THREE ELEPHANT BRAND

BORAX
BORIC ACID
PYROBOR

★

Li_2O

LITHIUM CARBONATE
LITHIUM HYDROXIDE
LITHIUM ORES

★

BORAX & CHEMICALS LTD.

KINGS BOURNE HOUSE

229 HIGH HOLBORN, LONDON, W.C.1

Telephone: HOLborn 6518

Telegrams: BORAXCHEM PHONE, LONDON

Cables: BORAXCHEM LONDON

SIGNS OF THE TIMES

THE fact that during the three days of the Conference of the Institute of Metal Finishing held at the Norbreck Hydro, Blackpool, last month, more than three hundred delégates and ladies were recorded on the register, and that this number included a not insubstantial overseas representation, must surely be taken as indicative of considerable interest in the technical fare provided. This is further borne out by the fact that the numbers present at the technical sessions were at all times satisfactory and the discussions following the presentations of the papers were lively and to the point. It reflects considerable credit on those responsible for putting together the technical programme that it proved sufficiently attractive to make the long journey to the North-West coast worthwhile for so many people.

It was interesting to observe as a sidelight on current trends of thought that the two sessions which obviously commanded the greatest amount of technical interest, and which were perhaps in themselves responsible for the presence of a number of delegates who had not previously attended one of these Conferences, were devoted to subjects other than electrodeposition.

It is perhaps not unnatural that a body of electroplaters, a major part of whose time is devoted to the electrodeposition of nickel, should evince great interest in a process whereby nickel can be deposited fully bright into the deepest recess without the need of an externally applied electric current and therefore the keen attention which was devoted to the exposition by Dr. Gutzeit of the process patented by his company for the deposition of nickel by catalytic chemical reduction was well founded.

Again, the livelihood of a large section of the electroplating industry is closely tied up with the continued use of nickel/chromium plating on motor-car trim, and any trend away from nickel/chromium plate in this application would not unnaturally be closely watched. This was apparent in the interest shown in the session devoted to methods of chemically and electrolytically brightening aluminium and, more particularly, in the paper in that session which described the extent to which aluminium so treated is being used on motor-cars in Germany.

Nickel/chromium plate has enjoyed a good run and although it has not been without its detractors, it has in the main given a very good account of itself. Just how good it is as an effective protective and decorative combination is evidenced by the notable lack of success which attended all efforts to find a satisfactory substitute for it at the time when the shortage of nickel threatened to curtail the extent to which it could be applied. Now it appears that an alternative material is about to challenge it strongly in its own right, claiming advantages of lower cost, greater ease of processing and reduced weight. In this country the battle has scarcely yet been joined and any attempt to prophesy its future trend or ultimate outcome would be premature, but the very existence of the threat can be taken as symptomatic of the times we live in.

New materials and new processes are becoming available today at a faster rate than ever before in our history and a process which is commonplace and widely accepted now can very easily find itself outmoded and superseded in a very short passage of time. Nickel/chromium plating has lent itself to automatic operation and there is in consequence a fair amount of capital represented by automatic plating plants designed for nickel/chromium deposition locked up all over the country. Such plants will not be written off hastily and the supporters of any new process will have to show very good reasons for its adoption before existing plants will be scrapped. On the other hand if the future demand is going to exist for finishes other than nickel/chromium the industry in this country cannot fall behind in the race to provide them. It is not really to be wondered at therefore that such interest was shown in the two forward-looking sessions of the Blackpool Conference to which we have referred.

Talking Points by "PLATELAYER"

TOPICAL COMMENT FROM THE MAIN LINES AND SIDE LINES OF METAL FINISHING

ADD BRIGHTNESS TO LIGHTNESS

AS practically every columnist has had something to say about the car industry and its present difficulties, it would be fashionable, if nothing else, for some comment to be made here also. Inundated as the motor industry is today with criticism and advice, (mostly ill-informed), from every quarter, I can feel confident that a little more will pass unnoticed.

A study of customer reaction in practically all the export markets for British light cars shows conclusively that colour and appearance are overriding sales considerations. Wherever two similar models appear, even of the same make, the one with the most chromium plate, the least drab colours and the longest line will always outsell the other, even when there is a substantial price differential between them.

In this country gaudy cars with a lot of plating may seem out of place, and not even to the taste of our indigenous stylists. The sixty-four dollar question then is, do we continue to make cars which the British public admire, but are officially discouraged from spending their money on, or shall we produce vehicles which are not to our own liking, but which our foreign customers want, and which it is in our interest that they should buy?

$(C_2F_4)_n$

A resin which is likely to become much better known in the not-too-distant future as a coating material is polytetrafluorethylene. Totally unaffected by any weather conditions, and inert to nearly all chemicals, both inorganic and organic, it can be used at temperatures of up to 400°F. (204°C.), so that its possibilities are evident in spite of its high cost. The main difficulty in the way of the application of P.T.F.E. in the finishing field is that there is no known material which will dissolve it, so that it is not possible to apply it from solutions in the usual way. However, aqueous dispersions containing up to 50 per cent solids have become available which can be sprayed or brushed onto metal surfaces and then baked on at high temperatures (360 to 400°C.). Bearings have been produced in this way by the impregnation of porous metals, the success of which is based on the low coefficient of friction of the material. Attempts to apply the material in this way to solid surfaces such as sheet steel, have, however, been baulked by the fact that little adhesion is obtained when the film has formed. Recently it has been found, however, that when the dispersions are mixed with chromic and phosphoric acids, a remarkable increase in adhesion is obtained, and dispersions of this type are becoming commercially available.

Q.E.D.

One might not have thought that the phenomenon of queueing was capable of mathematical analysis, but there is no limit to what the present-day mathematician is prepared to tackle. Yet the queue problem is an important one for industry as well as for the shop-keeper around the corner, as almost every organization is confronted with it all the time. Problems come along and have to be dealt with at irregular intervals, each one taking an undetermined amount of time; simultaneously more problems join the queue at the end, either singly or in batches. The difficulty arises from the need to ensure that unconscionable delays do not occur, whilst at the same time there should not be an unduly large reserve of personnel and equipment remaining unused. It is, therefore, evident that any useful information about queues can only be obtained on a statistical basis, and an interesting study of the subject has recently been published by R. K. Prince of the Lockheed Aircraft Corporation.

The Paradox of the Queue is that no matter how rapidly problems are solved, some will always be delayed by standing in the queue—often to somebody's consternation. This is because problems come at random intervals, and periodically a situation arises when a group of problems is so closely spaced that the last one arrives whilst the others are still being solved. As a practical example, even though the capacity for solving twice as many problems as are submitted is available, half of the problems will be subject to delays. The object of the study is to enable the results of a proposed course of action with the object of reducing waiting time to be predicted, and to enable an economic optimum to be selected.

If there are any companies who would like to fix the strengths of their drawing offices, estimating or inspection departments on a scientific and mathematical basis, I would commend them to read Prince's article; the mathematics are heavy going, but the conclusions are relatively straightforward.

THE INSTITUTE OF METAL FINISHING • 1956 ANNUAL CONFERENCE IN BLACKPOOL

Report of Technical and Social Activities

THE Annual Conference of the Institute of Metal Finishing has established itself as an event of major significance in the metal finishing calendar during the post war years, and over the past six years attendance at this function has steadily increased. This year's Conference was held at the Norbreck Hydro, Blackpool, where over three hundred delegates, including ladies, were accommodated. The Conference followed very closely the pattern established in previous years and the social programme included a Civic Reception by the Mayor and Corporation of Blackpool and the Conference Dinner and Dance.

On the technical side a strong programme was provided comprising 15 papers presented in five sessions. In addition to the normal conference sessions the opportunity was also taken for the presentation of the Third Hothersall Memorial Lecture, the medal lecturer on this occasion being Dr. W. A. Wesley, manager of the Research Laboratories, The International Nickel Co. Inc., at Bayonne, New Jersey. In his lecture, which he presented as recipient of the medal awarded to him for his outstanding work in the field of electrodeposition, Dr. Wesley took as his subject "Of Nickel Atoms, Ions and Electrons" in which he sought to apply recent theories of the electronic structure of the transition elements to explain the mechanism of dissolution of nickel.

A basic part of the nickel-plating process is the electrode reaction by which nickel dissolves, Dr. Wesley said, adding that this reaction is also significant because it is the primary step in the corrosion of nickel alloys.

The Mayor of Blackpool, Alderman C. Dunn and Mrs. Dunn supported by Mr. R. A. F. Hammond, president of the Institute of Metal Finishing, and Mrs. Hammond, stand ready to welcome Conference delegates to the Civic Reception in the Winter Gardens.

PERSONALITIES AT THE CIVIC RECEPTION

Top frame, left to right.—Mr. R. M. Angles, Tin Research Institute; Mr. A. W. Spaven, Percival Aircraft Ltd.; W. E. Cattley, The Walterisation Co. Ltd.; Mr. R. R. Benham, Johnson, Matthey and Co. Ltd.

Second frame, left to right.—Mrs. H. Silman, Mrs. A. W. Wallbank, Mrs. G. A. Jordan, Mr. H. Silman (Electro-Chemical Engineering Co. Ltd.); Mrs. A. C. Benning, Mr. G. A. Jordan (G. A. Jordan and Co. Ltd.), Mr. A. C. Benning (Harshaw Chemicals Ltd.).

Third frame, left to right.—Mr. D. Powell, and Mr. R. A. Wilding, Bristol Aero Engines Ltd.; Mr. D. Jackson, The Staveley Iron and Chemical Co. Ltd.

Fourth frame, left to right.—Professor J. W. Cuthbertson, Nottingham University; Mrs. J. W. Cuthbertson, Dr. W. A. Wesley, The International Nickel Co. Inc.; Mrs. R. A. F. Hammond.

In spite of the importance of the reaction, the mechanism by which it takes place is not fully understood and the behaviour of nickel as demonstrated by its polarization curves requires more explanation. In a field somewhat remote from electrochemistry, namely, that of solid state physics, recent advances have brought forth new ideas regarding the electronic structure of metals. These ideas have given Dr. Wesley what he believes to be the key to an explanation of the behaviour of nickel anodes in nickel-plating.

He proposed in his lecture a theory that the electronic structure of the nickel atom, as it is believed to exist in the metallic state, plays a decisive part in the mechanism of the reaction by which nickel dissolves. If the three kinds of nickel atom cores which exist in nickel metal require different energies of activation for reaction, then this can be used to explain most of the unusual features of the behaviour of nickel anodes which have puzzled electrochemists for decades.

The theory should also lead to new developments in the practical as well as the scientific aspects of the nickel-plating process. It is expected to stimulate research in the field of corrosion and there is reason to believe, Dr. Wesley remarked, that some puzzling features of the corrosion and passivity of not only nickel but other metals and alloys will be explained when they are examined in the light of his theory.

Among the many excellent papers presented during the technical sessions two occasions were particularly noteworthy. The first technical session was devoted to consideration and discussion of chemical and electrical methods of brightening aluminium prior to anodizing and the possible applications of the metal thus finished in lieu of nickel chromium plate, particularly on motor car trim. The four papers presented at this session were admirably introduced by Mr. J. C. Bailey.

At the final session of the Conference the first dissertation in this country on the deposition of nickel by catalytic chemical reduction was delivered by Dr. G. Gutzeit of The General American Transportation Corp. who have made the process commercially available under the trade name "Kanigen."

At the Conference Dinner the Institute was proud to honour a number of distinguished guests, including the Mayor of Blackpool, Alderman C. Dunn, J.P., who responded to the toast of the Corporation proposed by Mr. B. J. Jones, chairman of the North West Branch of the Institute, who with Mr. H. Maxwell, Secretary of

the Branch Committee, had been primarily responsible for the local organization of the Conference. The toast of the Institute of Metal Finishing was proposed by Mr. R. P. Bell, F.R.S., President of the Faraday Society and responded to by the President of the Institute of Metal Finishing, Mr. R. A. F. Hammond. Mr. G. L. Bailey, director of the British Non-Ferrous Research Association replied on behalf of the guests to the toast proposed by Dr. T. P. Hoar, vice-president of the Institute.

One feature of the Conference Programme, which has now become an annual event and commands increasing support each year, is the contest for the John Preston Golf Trophy, won this year by Mr. W. K. Bates, manager of the metal finishing department of Albright and Wilson Ltd., with Mr. Cyril Wharrad, director of Britachrome Co. Ltd., as runner up.

A full programme of entertainment for ladies during the period of the Conference was arranged and provision was also included for parties to visit certain works in the neighbourhood during one afternoon.

From almost every point of view the Conference can be reckoned as one of the most successful yet staged by the Institute of Metal Finishing, and at the technical sessions a very good standard of attendance and discussion was achieved as will be apparent from the report of the highlights of the discussion which appears below.

Abstract No. 1:

Alkaline Electro-brightening and Anodizing of Aluminium.

By N. D. Pullen, F.R.I.C., and B. A. Scott, Ph.D., A.R.C.S., F.R.I.C., F.I.M.

THE paper reviews the present state of development of an established process for electrobrightening aluminium and points out that it is different to the normal bright-dipping treatments. An advantage of the electrobrightening method over bright-dipping is that the alkaline phosphate solution used is less corrosive and dangerous than any of the bright-dipping solutions which contain free hydrofluoric acid.

In the electrobrightening method the metal is subjected to anodic treatment at 12 volts d.c. in a hot alkaline electrolyte which brightens the surface but gives no additional anti-corrosive protection. A protective oxide film is applied later by the normal anodizing technique.

Best results are given with super-purity metal containing 99.99 per cent aluminium but almost identical results are obtained with certain super-purity aluminium alloys containing up to 1½ per

THE JOHN PRESTON GOLF TROPHY
PRIZE WINNERS

Receiving their awards from the hands of Mrs. Hammond and the President are: Top to bottom: This year's trophy winner Mr. W. K. Bates, Albright and Wilson Ltd. Second prize winner Mr. C. Wharrad, Britachrome Co. Ltd. Third prize winner Mr. R. G. Hughes, Electro-Chemical Engineering Co. Ltd., and consolation prize winner, Mr. F. G. Furniss, Electric Construction Co. Ltd.

cent magnesium. The advantages of these alloys is that they have greater mechanical strength and hardness.

The brightening process is carried out in a solution containing 15 per cent wt./vol. anhydrous sodium carbonate and 5 per cent wt./vol. anhydrous trisodium phosphate at 80-82°C. In a more recent development of this process, however, good results have been obtained using a solution containing up to 30 per cent carbonate and 6½ per cent phosphate. Etching begins almost immediately and is allowed to carry on for 10-30 seconds, depending on the metal purity. 12V d.c. is then applied between the stainless-steel cathodes and the aluminium anode. There is an initial surge to 35 amp. per sq. ft. which falls to 20 amp. per sq. ft. The treatment takes from 5 to 15 minutes depending on the metal purity.

Whitish streaks, " gas flow marks," will spoil the surface if the bath is stirred during the brightening process. The slight gas flow from the anode appears to improve the brightening process to a point and the lower surface of flat sheets treated at an angle of 45 deg. are generally brighter than the upper surfaces.

After treatment and washing a thin oxide film remains and if it is allowed to dry it will leave a friable outer layer after subsequent anodizing which will mark very easily; even finger marks will show as white streaks.

The method used to remove this film is to dip the article, before anodizing, into a boiling solution of phosphoric acid and chromic acid, 7 per cent by volume and 4 per cent wt./vol. respectively in distilled water.

The article is finally subjected to the normal protective anodic treatment in sulphuric acid, rinsed in water, sealed, dried and waxed to give extra protection against marking and to improve the " feel " of the surface. The anodic film may be dyed by immersion immediately before the sealing stage.

In preparing a new bath of electrolyte it is preferable to use less phosphate at first and to work at a slightly lower temperature to reduce the activity of the freshly made solution. This activity is due to the liberation of the hydroxyl ions by the hydrolosis of the carbonate and the phosphate, the latter being strongly alkaline in reaction. It is undesirable to use the tank as a cathode because the gas flow would disturb the solution. Wood or mild-steel baffles should be fitted in front of the cathodes and into the solution itself to prevent localized agitation which would cause stains on the metal being treated.

Consideration is given in the paper to the theoretical aspects of the mechanism of the electro-brightening process.

Total reflectivity and specular reflectivity of electro-brightened and anodized aluminium are high. The reflectivity being 84.1 per cent and the ratio of specular to the total being 0.994. Even after exposure to an industrial atmosphere there is little or no deterioration in surface finish.

The heat reflectivity is also high and it can be increased further by heating the articles in air at 160 to 170°C. for ½ to ¾ hr. so eliminating the hydration of the anodic oxide film which occurs during sealing in hot water. This avoids the deep absorption band for infra-red radiation in the 3 micron region due to -OH grouping.

Electro-brightened and anodized aluminium is used for reflectors where high reflectivity and corrosion resistance are needed, e.g. searchlights, aircraft landing lights, and radiant heaters. It is also used for decorative purposes such as costume jewellery, motor cars and fountain pen tops. The wide range of anodizing colours is a particular advantage here.

Abstract No. 2:

Some Studies of Phosphoric-Acid-Based Chemical Brightening Solutions for Aluminium.

By A. W. Brace, A.I.M., and T. S. De Gromoboy, B.Sc.

THIS paper is concerned with a series of electrobrightening tests carried out using commercial purity aluminium to discover the effect of the aluminium content of the brightening bath and also the effect of temperature on the amount of metal removed. Four different acid solutions were used and the results obtained were collated and analyzed.

This study resulted from the fact that there is a loss of reflectivity when mechanically polished aluminium is anodized. Electropolishing can be expensive because of large drag-out losses and the high current densities required and so the investigation concerned itself with chemical brightening because of its simplicity of operation and its ability to give good results on commercial purity aluminium.

Most chemical brighteners are based on orthophosphoric acid with the addition of other acids such as sulphuric, acetic, boric and nitric.

In the first series the brightening solution consisted of phosphoric-sulphuric acid in the ratio of 75 per cent to 25 per cent by volume. The solution was heated to a temperature of 100°C. and the commercial purity aluminium was immersed and hand agitated to prevent surface streaks due to gas bubbles, drained, plunged in running water and then dried in hot air. The effect of the time lag between removal from the brightening bath and quenching in water was also studied. The reaction continued after removal

from the brightening mixture and before quenching and this increased the amount of metal removed but it did not affect the surface appearance. The aluminium content of the bath gradually increased with the following results. The initial aluminium content was 5.68 gm. per litre, and the increased content did not have any appreciable effect on the solvent power of the solution for about two thirds of its life and then there was a gradual falling off in the amount of metal removed. This could be compensated by increasing the temperature of the solution. When the content reached 19.3 gm. per litre the surface quality deteriorated.

The brightest surfaces were obtained when the temperature was between 95 and 100°C. Above this there was a tendency for pitting and, below, etching occurred.

Similar tests were recorded with all the other mixtures and the results were as follows.

Phosphoric-sulphuric-nitric acid in the proportions of 75-20-5 per cent by volume gave a similar result to that of the first test as regards the effect of delay in rinsing on the loss in weight.

When the aluminium content reached 6.2 gm. per litre the surface became etched and stained but with the addition of 50 ml. of nitric acid the bath was restored to working conditions. It was necessary to add further nitric acid when the aluminium content reached 8.4 gm. per litre and when it had reached 11.89 gm. per litre neither additional nitric acid nor increased temperature restored the brightening power of the bath.

When the temperature rose to 110 to 120°C. there was a tendency for an undulating surface to be produced.

With a solution of phosphoric-acetic-nitric acid in the proportions of 75-20-5 per cent by volume a time lag of only 1 second was allowed between removing the metal and rinsing. It was necessary to add 5 per cent of nitric acid when the aluminium content reached 6.88 gm. per litre. The specimens were not as good as those treated in the previous solution for they had a more diffuse brightness.

In contrast to the results obtained with the other solutions is the fact that although the rate of solution increases with an increase in temperature the increase becomes less marked as the temperature is raised.

Using phosphoric acid-water-nitric acid in the proportions of 75-20-5 per cent by volume at a temperature of 100°C. the first signs of deterioration occurred when the aluminium content reached 5.9 gm. per litre. 30 ml. of nitric acid were added and again when the content reached 7.5, 12.73, and 18.7 gm. per litre. When the aluminium content reached 20.5 gm. per litre neither the addition of more nitric acid or an increase in temperature had any effect. The effect of the temperature on the amount of metal removed is similar to that of the sulphuric-nitric mixture and confirms 100°C. as the best operating temperature from the aspect of surface appearance, although it may be necessary to increase it to 110 to 115°C. in the case of an old bath.

A further experiment was carried out using the same mixture as before but accidentally the phosphoric acid was only the technical grade so that the proportions became 51-44-5 per cent; a similar solution was used containing 0.25 per cent by weight of copper sulphate. This second mixture gave a better result and also dissolved less aluminium. However when pure phosphoric acid was used the results failed to confirm the beneficial effects. It is thought that the presence of copper in conjunction with the lead impurity in the technical acid was responsible.

A test was made of the chemical polishing characteristics of different grades of aluminium and its alloys using the same polishing solutions as previously investigated. The metals used were NS4 (anodizing quality), HS10WP, HS15W, S1C (99.2 per cent A1), S1B (99.5 per cent A1-anodizing quality), S1 (99.99 per cent A1-anodizing quality), and SP12 (A1 99.99 per cent —1.25 Mg.). The brightness results improved with the purity of the metal but none of the solutions gave satisfactory results with HS15W; further, HS10WP did not give as good a result as the other commercial purity metals.

The results showed clearly that in the phosphoric-acid mixture there was a relationship between the loss in weight and the time of immersion and with the substitution of nitric acid for part of the sulphuric acid the amount of metal dissolved was much less under similar circumstances. This is due to the formation of a porous oxide or hydroxide layer and to the rate of film formation being in equilibrium with the dissolution rate.

With acetic in place of sulphuric acid the tendency for the rate of solution to increase with a rise in temperature was reduced, and this rate was lower than for any of the other mixtures.

The phosphoric acid-water-nitric acid mixture gave a slightly higher rate of attack than the other two compositions.

The maximum aluminium content is of great economic significance and here the phosphoric acid-water-nitric acid mixture which reached 20.5 gm. per litre of aluminium was the best.

All except the phosphoric-acetic-nitric acid mixture showed a sharp increase in the rate of attack over the range 105 to 120°C. The acetic acid reduces the danger of unduly violent attack due to any unexpected rise in temperature.

The results of the response of various alloys to

chemical brightening showed that as the purity increased so did the loss in weight, but the addition of magnesium lowered this weight loss.

The investigations have shown that various phosphoric-acid mixtures can brighten aluminium and its common alloys but that with some of the mixtures the appearance is mainly diffuse. However, for a really specular finish the presence of nitric acid is essential.

Abstract No. 3:

Studies in Bright Anodizing by the Ammonium Bifluoride-Nitric Acid Process.

By G. E. Gardam, Ph.D., A.R.C.S., F.R.I.C., F.I.M., and R. Peek.

THIS paper outlines the properties of chemically brightened aluminium in particular its high reflectivity and its high resistance, when anodized, to atmospheric corrosion.

There are three factors which help determine the merits of the brightened surface and by which its quality is judged, *viz.*: the total reflectivity, which if low imparts a dark or grey colour; the absence of diffuse reflectivity, bloom or haze, the presence of which impairs the impression of brilliance; and the sharpness and clarity of reflected images, without which even the most brilliant surfaces appear of poor quality.

Various chemical brightening processes are described and their faults and merits discussed. A process widely used on the continent but new to England is also explained in detail and the preparation of the electrolyte, the application of the process and typical results are given.

The solution consists of nitric acid, ammonium bifluoride and lead nitrate in the proportions of 13-16-0.02 per cent wt./volume. Super-purity aluminium or its magnesium alloys treated in this solution for 15 to 30 seconds at a temperature of 50-80°C. are given a high lustre. If these conditions are not fulfilled the surface acquires a matt finish. The rate of attack is rapid and 0.002 in. is removed in 15 to 30 seconds. Consequently there is no need for any pre-polishing treatment. However, the final image clarity is rarely as good as a mechanically polished article.

In a solution of ammonium bifluoride and nitric acid the amount of metal removed is closely proportional to the immersion time and the rate of attack is only slightly dependant on the nitric-acid content. When the ammonium bifluoride rises above 7 per cent the rate is closely proportional to this percentage minus 4 per cent. As the rate of attack increases so the image clarity decreases and the surface undulates slightly, this "pebble" effect remaining in more concentrated solutions even if the nitric acid and the ammonium bifluoride are present in the correct ratios.

At the higher concentrations of ammonium bifluoride and nitric acid a deficiency of nitric acid causes a white irregular stain in the period between removal from the bath and rinsing.

The addition of lead nitrate to a pure solution of 13 per cent ammonium bifluoride and 12 per cent nitric acid (both wt./vol.) gave good bright results when the percentage was between 0.02 and 0.075, but above this the surface became undulating. Since commercial ammonium bifluoride contains lead it will give good results and when the lead content becomes too high it can be removed by electrolysis between graphite electrodes.

A test was made with the addition of another heavy metal, copper, as copper nitrate, to see if it would function similarly, but no successful results were obtained.

Additions of hydrofluoric acid, ammonia, boric acid and silicic acid were tried but none produced good results and there was a general deterioration of the brilliance and image clarity.

In the range 50 to 60°C. no marked effect of temperature was noticed on the results obtained, but it is believed that higher temperatures would increase the rate of attack and cause loss of image clarity.

It was calculated that a solution containing 16 per cent ammonium bifluoride will brighten 236 sq. cm. of aluminium per litre before precipitation occurs. However, the bifluoride content can drop to 13 per cent without detriment to the polishing efficiency and this is equivalent to a treatment of a further 460 sq. cm. per litre before replenishment is necessary. Replenishment is effected by adding ammonium bifluoride to bring the solution back to its condition before precipitation commenced; this however adds lead impurity to the solution. Nitric acid and lead are lost only by drag out, the dissolved aluminium continuously precipitates out and the process appears to be capable of regeneration, theoretically, without limit.

Vigorous reaction continues to take place after removal from the brightening bath and it is possible that the articles will have a surface film of lead. They should be rapidly rinsed in running water and then dipped in a 50 per cent solution of nitric acid otherwise staining will occur. If anodizing does not follow immediately then they should be put in a holding bath of 1 per cent potassium dichromate or chromic acid.

The anodized coating should be compact for good transparency, hard enough to resist abrasion and be at least 10 microns thick. Only the sulphuric-acid method will give a colourless transparent film, but a more dilute solution, operated at a lower temperature and a higher voltage is preferred. It can be easily sealed by immersion in boiling distilled or de-ionized

water for 20 minutes.

The anodic coating is formed by the conversion of slightly thinner layer of metal into oxide and the surface smoothness is not disturbed if the metal is sufficiently pure. Any impurities, such as iron, titanium or silicon, will affect the brightness, clarity and reflectivity.

Abstract No. 4:

Chemically Brightened and Anodized Aluminium and its Employment in Automobile Manufacture.

By F. Baumann, Dipl. Phys. and H. Neunzig.

THIS paper gives an account of the use being made by the German automobile manufacturers of chemically brightened and anodized aluminium for car fittings. Since its introduction by Volkswagen three years ago on a minor scale it is being used more and more, and now Mercedes-Benz, Porsche and Goliath cars are using it as well. Anodized aluminium is being used to replace parts that were formerly made of chromium-plated brass.

During the brightening process there occurs a levelling of surface roughness, with the metal on the high points being dissolved faster than that in the valleys. The authors have formed the opinion that the essence of the brightening process consists not in the levelling of the geometric surface roughness but, on the contrary, in the prevention of an etching type of attack.

In anodizing, an adherent passivating film is built up on the surface and the reaction can only occur through defects in this film, which acts as a buffer and so etching is prevented. This surface film obscures the contours of the metal as its thickness increases so it should not be allowed to exceed a certain thickness otherwise the smoothing action is diminished. For this reason only a slight levelling action occurs during anodic oxidation even though etching is prevented.

The ammonium fluoride-nitric acid bath is very sensitive to metal impurities because there is no continuous buffer film formed. The specular reflectivity of a piece of hard-rolled material containing 0.05 per cent iron immersed in this low-viscosity solution was depressed from 84 to 71 per cent yet when treated in a bath with a high-viscosity phosphoric acid, it remained constant. The fluoride-nitric acid bath reacts even more sensitively to impurities of copper and nickel than to iron.

The high reaction rate and proportionally high rate of attack on the metal has its advantages in that it obviates the need for prior polishing of the surfaces. It is also economic and easy to operate.

The choice of material is very limited however, and only super-purity aluminium, 99.99 per cent, and its magnesium alloys up to 2 per cent can be used.

To achieve a brilliant finish without trace of texture, the strip should be annealed for about 4 hours at 300 to 320° C. before the final temper.

In the operation of the process the components are polished, set in racks and hand immersed in the brightening bath which contains nominally nitric acid, ammonium bifluoride and lead nitrate in the proportions 13-16-0.02 per cent wt./volume. At a temperature of between 50 to 80° C. the brightening takes 15 to 30 seconds. The procedure after withdrawal is the normal one, *viz.* rinsing, dipping in 40 per cent nitric acid and rinsing again. Anodizing is carried out in a 21 per cent by weight sulphuric-acid electrolyte treated with a foam-forming wetting agent. It is better to seal with steam than hot water.

On strip, if the annealing temperature is too high or low or the time too short then matt regions or an " orange peel " surface will be produced during subsequent forming operations. With extruded material the tools must be very smooth otherwise there will be a danger that the parts will need polishing before brightening because the bath is not capable of relatively great levelling to smooth severe roughness.

Too much nitric acid in the bath produces a blueish tinge and too little causes dullness.

Two processes which are used in the automobile industry for rapid testing of the quality of the anodic films are explained. In the Kesternich method the anodized parts are exposed to an artificial industrial atmosphere in an airtight vessel. This shows whether there was too high an electrolyte temperature, insufficient sealing, insufficient clearing, etc.

The other test which uses an oxidizing solution of common salt acidified with acetic acid is a corrosion test and indicates not only the thickness of the film but also the composition of the base metal, since the reagent has a pronounced reaction in depth. This method shows that for standardization of the lowest possible anodic film thickness for different conditions of application, not only the oxidation process but also the metal quality must be borne in mind.

Discussion

Mr. I. WALKER (Briggs Motor Bodies, Ltd., Dagenham), said that the motor industry was particularly interested in investigating the possibilities of using brightened aluminium to replace chromium-plated parts in the hope of getting increased durability, less cost and less weight, and to assist in avoiding the ever-present danger of a potential nickel shortage. The main interest was in a bright anodized finish to match

the present chromium-plated finish.

In the paper by Pullen and Scott it was claimed that a high degree of image clarity was of only minor importance, and suggested that it should only be necessary to remove major surface irregularities such as spinning marks. Did the authors consider that alkaline brightening would give high specular reflectivity and image clarity without mechanical polishing if it were assumed that the original metal surface was free from major surface irregularities? If some mechanical polishing was required, would they define what they meant by "polishing"?

The authors referred to a more recent development of a process containing a solution with 30 per cent carbonate and 6½ per cent phosphate. Had they any further information on this new solution, and did it give superior results to those obtained with the solution used in the process described in the paper?

The authors stated that deionized water must be used for anodizing and distilled water for sealing. Had they any information on the amount of impurities which could be tolerated, because the water would be pure only until the first components were swilled?

It was suggested that preliminary mechanical polishing might be omitted when the metal surface was good. What was meant by a good surface finish, and could it be maintained as a production-rolled finish? Also, to what extent did the authors consider that waxing of the sealed anodic film was necessary? They said that it afforded additional protection against finger marking and other corrosive influences, but a satisfactorily sealed film should give adequate protection.

In the paper by Gardam and Peek the authors commented that full image clarity demanded mechanical polishing. It would be interesting to know whether they had any explanation of this, since as much as 0.002 in. of metal was removed by the brightening process, which should remove any surface effect of the polishing. They mentioned that " orange peel " or " pebble " was the chief defect of the process. Did they consider that it was a practical proposition to brighten a large number of parts having large surface areas or varying angles, bearing in mind the possible non-uniformity of attack? Passing reference was made to the unsuccessful results obtained with the addition of copper instead of lead. Had they any further information on that subject, and did they consider that a practical limitation of the process was the possible build-up of copper in the solution?

There seemed to be a slight difference of opinion between the authors of the third and fourth papers with regard to the advisability or otherwise of steam treatment for sealing. It would be interesting to hear the comments of both sets of authors on this point.

Finally, the authors referred to the rather alarming maximum impurity limits for the production of a satisfactory finish. Did they consider that it was a practical proposition to manufacture production quantities of super-purity aluminium base alloy sheets with less than 0.002 per cent iron, no titanium, less than 0.01 per cent silicon, and no insoluble intermetallic compounds or aluminium oxide?

In view of the known difficulties of the process, it was refreshing to read the fourth paper by Baumann and Neunzig, on the now extensive use of chemically-brightened and anodized aluminium in Germany. These authors mentioned, however, that components for automobiles were first polished and then wiped off with Vienna lime, if considered necessary. It would be interesting to know how much polishing was considered necessary and how extensively this had to be conducted, and also what type of abrasion test was conducted in Germany, particularly in view of the fact that in Germany a thickness of anodized film of 4-7 microns was considered to be satisfactory, whereas the minimum considered necessary in this country was 10 microns.

He would like to give some idea of the thoughts in the motor industry about the type of specification which would be necessary to ensure that the products were satisfactory. The thickness of anodic coating should be a minimum of 0.0004 in., but not more than 0.0005 in., because of the danger of cracking. It was possible that further evidence about these finishes would make it possible to lower those limits so as to bring them more into line with the present German standards of 4-7 microns, but the motor industry did not feel able to make this move without further service experience. For the resistance to abrasion tests, they asked for four times the resistance of the chromic acid film, in the hope that the development work to provide a suitable abrasion test apparatus would be completed before the specification was in full use. They were proposing to inspect the characteristics of a brightened and anodized surface by comparing it with a master sample. The wording which they proposed for the specification was as follows:

> " The specular reflectivity, the total reflectivity and the image clarity of the brightened and anodized surface shall be at least equivalent to those of the previously accepted master sample part. A 2-in. square flat specimen

shall be produced from the same material and at the same time as the master sample part. The total reflectivity of the 2-in. square flat specimen shall be of the order of 80 per cent, of which the specular reflectivity shall be not less than 98 per cent when tested in accordance with B.S. 1615."

For sealing, the only tests available at the moment were those in B.S. 1615, and there was some evidence that they were not entirely satisfactory. The resistance to corrosion clause, 200 hours salt spray, should cause no concern. In conjunction with the British Non-Ferrous Metals Research Association, the motor industry were collaborating to devolop a SO_2 test. When this work had been completed, the specifications would be revised and the present sealing and resistance to corrosion clauses amended.

Mr. A. WALMSLEY (Burco, Ltd., Burnley) said he would like to have more information on sealing methods, steam *versus* boiling water, both from an economic point of view and from the point of view of efficiency. It was impossible to over-emphasise the importance of the sealing of an anodic film. He found that the *p*H value of the sealing bath was an excellent measure of its efficiency; if the *p*H was allowed to fall below 5, which it would do very quickly, the sealing was useless. The nickel-acetate method, with which most people were by now familiar, was also subject to this defect; the *p*H must be controlled. He thought that the *p*H of a steam bath would not be affected so that it would be much more efficient, but he would like the authors to comment on that.

Mr. H. J. BACHE (Electro-Chemical Engineering Co., Ltd., Weybridge) said that Pullen and Scott mentioned that periodical replenishment of the electrolyte was required to make good the drag-out losses. Could they state, for a 40-hour week, what frequency of replenishment was necessary? Was it daily, weekly or monthly? They also said that in the anodic process a lead-lined tank was required for the electrolyte. He presumed there was no objection to using a rubber-lined tank.

On the subject of rinsing he asked whether the size of the rinse tank was really material provided that, as for example in a mechanized process, the rinsing was adequately carried out.

Again, still bearing in mind the possibility of mechanizing the process, was it necessary when treating an object which was more or less circular or spherical in shape, for the article to be turned after the process had been carried out for part of the time, in order to make more uniform the brightening effect on both the upper and the lower surfaces?

Mr. F. SACCHI (Instito Sperimentali dei Metalli Leggeri, Novara, Italy), in the course of a number of comments discussed the effect of aluminium content on bath behaviour. Brace and de Gromoboy had found that after the aluminium content had reached 6.2 gm. per litre the finish deteriorated, and additions of HNO_3 had to be made until at 11.98 gm. per litre such additions ceased to be effective. In his laboratory they had tried to follow more closely the ageing of a bath of this kind by analyzing the solution after known surfaces had been treated. Their findings were that although it was possible to have good results over a wide range, optimum results could be obtained only within rather strict limits, such as between 10 and 15 c.c. per litre of HNO_3.

They also concluded that a replenishing solution could be safely formulated to maintain the bath at its optimum efficiency.

Dr. T. P. HOAR (Cambridge University) said that the business of brightening aluminium had been rightly referred to by Mr. Bailey as an art, who had twice referred to the lack of scientific knowledge of the mechanism of these processes. It was interesting to find that in the four papers there was only one short discussion of mechanism, and that was in the paper by Baumann and Neunzig, who gave what was probably the commonly accepted view that brightening and polishing were different, and that brightening was due to random deposition. When Dr. Hoar and Mr. Mowat brought forward that idea in 1951 it had been regarded as rather funny, but now it was just " old stuff," and that was very gratifying.

At the same time, all these ideas about theory remained perhaps not speculative but certainly qualitative, and what was required for further advance in this field, as in so many others in metal finishing, was a much clearer quantitative idea of what the electro-chemical processes which took place really were. He hoped that the present discussion would stimulate Dr. Gardam and others to make a proper study of mechanism, just as they had made a very good study of the results from a practical point of view. If the process in question was to become a real competitor of certain other processes which no longer enjoyed their old popularity, Dr. Hoar was sure that further advance from the present state of the art must be based largely on a much clearer scientific appreciation of what went on.

There were two points in particular to which consideration should be given. The first was the mechanism of chemical polishing in which it was likely that more than one mechanism was involved.

The other point was that of sealing, where there was a great deal to be discovered from the

point of view of making a film which was corrosion-resistant. If sealing could do that, it was an extremely important part of the entire process. It remained to be seen whether steam or boiling water or something else was the real answer to the sealing problem. The study of the various variables involved would lead to the answer.

Mr. J. M. KAPE (High Duty Alloys Ltd., Slough) put in a plea for more attention to be paid to the possibilities of using commercially pure aluminium. He did not think that that material had been sufficiently investigated so far as its brightening and anodizing properties were concerned. Very little work had been done on the testing of these commercial-purity films, and no comparison had been made between a super-pure material anodized to a very thin film and a commercially-pure material anodized to a very thin film, with regard to reflectivity, corrosion resistance or abrasion resistance.

Mr. J. F. KAYSER (Gillette Industries, Ltd., Isleworth) said that the phosphoric-acetic-nitric acid mixture was a most reliable one in his experience and gave no trouble whatever. His company had used it since 1950, and in that time had treated hundreds of millions of parts. They used an 80 : 15 : 5 mixture at 75-80°C, and an essential ingredient was a wetting agent. After every 5,000 pieces they made an addition of nitric acid and wetting agent, and after every 10,000 they topped up with the basic acid. One of the original stainless steel tanks, put into operation in 1950, was still in perfect condition.

Mr. C. E. MOORE (Ashton & Moore, Ltd., Birmingham) said that the importance of knowing something of the mechanism of sealing was apparent not only for brightened aluminium but for all anodized aluminium. There seemed to be some conflict of opinion about whether hot water or steam sealing was preferable. He would suggest that perhaps the difference might be due to the extent to which sulphuric acid had been leached out of the film prior to sealing by the two methods. He would like to ask the authors whether they had considered the effect of such leaching and whether it would have a determining influence on whether steam sealing in particular would be efficient or not.

He would like to know from the exponents of the bifluoride method whether any health hazard or nuisance was attached to that process, which dissolved metal at a very great rate and therefore presumably produced considerable gas and spray. Mr. Bailey had said that there was no fume, but was there an acid spray hazard to health or a nuisance to the operator or other persons engaged in the immediate vicinity?

Mr. H. LOW (The National Cash Register Co. Ltd., Dundee) supported Mr. Kape's appeal and enlarged on it. It was necessary, he thought, for some work to be done on brightening and anodizing casting alloys, and particularly die-casting alloys, because that was a field which lent itself particularly to the mass production of components and the brightening and anodizing of components made from these alloys had up to now not shown much promise.

He had one question to put to Pullen and Scott. In their nickel-acetate sealing bath, what materials did they use for the lining? He had had experience, he said, with lead-lined tanks and the rate of heat transfer had been unsatisfactory. He had used stainless steel coils with much better results. He used a 10 per cent nickel-acetate solution, and it seemed that during off periods a certain amount of salt tended to crystallise out on the tank, and there was some difficulty in redissolving it in a reasonably short period.

Mr. R. W. NUTTALL (Northern Aluminum Co., Ltd., Banbury) said that his company had been doing a good deal of work on the possibility of using emery scurfing instead of a full polish, particularly for the Erftwerk process. They found that 180-mesh emery was reasonably satisfactory, with occasionally a few slight scratches. By using 220 or 240 mesh he thought that there would be no trouble at all.

Dr. Gardam had asked him to answer the question relating to impurities and metal supply. He thought that those who used aluminium for trim could neglect any problem with the Erftwerk process arising from impurities. Mr. Walker had expressed concern about the levels of impurities which Gardam and Peek mentioned, such as 0.002 per cent iron. Since that paper was written a considerable amount of further work had been done in Banbury on this subjcet, and the level which they specified at the moment was a maximum of 0.005 per cent iron and 0.007 per cent silicon. In fact, carrying out analyses on finished material the highest quantity of iron present in any of their experimental material had been 0.005 per cent, which was exactly on the specified limit, while for silicon the figure was 0.006 per cent. The average had been 0.003 per cent in both cases, so that most of the material was well within the satisfactory specification, and all of it was within the maximum.

Mr. Kape had raised the question of the use of commercial-purity material. Mr. Kape was perhaps a little unfair in saying that there had been very little testing on thin films, and Mr. Nuttall hoped that Dr. Gardam would give some of his test results on exposure of thin films of

commercial-purity and super-purity material. A good deal of testing had been done. It was known that super-purity material behaved much better with a thick film than with a thin one, and there was no reason to suppose that commercial quality would be any better with a thin film than was the super-purity material. The feeling in the aluminium industry was that the use of thin films of 2-4 microns for outside exposure was very dangerous, because they were liable to early breakdown, and they would not do the car industry or any other users, or for that matter the aluminium industry, any good at all. Care should be exercised before considering commercial-purity material which could be brightened, because it was not possible to have a thick film, in order to obtain abrasion resistance, without getting a very dull finish.

He would like to ask Baumann and Neunzig whether they found that recrystallization of material was necessary for brightening. At Banbury experiments had been carried out with recrystallized and uncrystallized material, without establishing a clear answer. Secondly, had Baumann and Neunzig carried out any experiments and obtained any successful results with castings in the same type of alloy, *i.e.*, super-purity aluminium with magnesium additions?

In reply to Mr. Walker's question whether the aluminium manufacturers could supply consistent material, the answer was that they could certainly do so and were doing so now; and he did not speak only for his own company in saying that.

Dr. F. A. CHAMPION (The British Aluminium Co., Gerrards Cross) on the question of the exposure of brightened and anodized parts, said that he and Mr. Spillett had presented a paper to a recent S.A.S.M.U.T.A. Conference which had been published in the January issue of *Sheet Metal Industries* and contained a table giving the results of exposure in an industrial atmosphere for 7 years and in a marine atmosphere for 11 years of three grades of pure metal, of 99.5, 99.8 and 99.99 per cent purity. The four new films in that table had been electro-brightened by the Brytal process. Also in that paper photographs were given of trim in the super-purity magnesium alloy, electro-brightened and anodized. The vehicle in question had been in service for two years, and the trim was still in excellent condition.

Mr. D. R. NEWMAN (Electro-Chemical Engineering Co., Weybridge) said he had noticed in all the samples of anodized and brightened aluminium which he had examined that, irrespective (within reason) of the film thickness the oxide coating was extremely brittle, and the slightest flexing gave very fine hairline cracks. He would like to ask Baumann and Neunzig in particular how this cracking, which he thought must occur in the life of the material on the motor car, affected the specular reflectivity and the total reflectivity with exposure time.

Authors' Replies

Dr. B. A. SCOTT, replying to the discussion said that Mr. Walker had raised the question of image clarity in connexion with a reflecting *versus* a decorative finish. A searchlight reflector was an example of a case in which image clarity was of paramount importance. On the other hand, for a small decorative article, such as a pen cap or a portion of motor car trim showing a curved surface, image clarity was not so important, because in any case it was broken up by the nature of the curvature of the surface, and therefore polishing beforehand was less necessary.

Mr. Walker had asked him to define the kind of polishing which the authors recommended, and all that they recommended for the best finish was an extremely light polish with a fairly soft mop. So far as the question of treating by the alkaline process metal articles which had not previously been polished was concerned, it was quite possible to do this and obtain quite a good finish, showing good image clarity. He had seen samples manufactured from the as-produced sheet without any mechanical polishing, which had been treated by the alkaline brightening process and achieved an extremely good finish from the point of view of image clarity. On the other hand, the ammonium bifluoride process without polishing produced a grain finish, a sort of proto-orange peel which impaired image clarity and was suitable only for decorative articles.

Reference had also been made to the additional strength of the 30 per cent carbonate solution mentioned in the paper. They had used that, and it worked. It was used on the Continent, and he had included it on that account, giving a reference to the paper. The reflectivity figures were closely comparable with those obtained with the normal strength solution. The disadvantage was that the bath crystallized out on cooling and if allowed to stand all night it was a problem to heat it up again.

On the question of deionized or distilled water, Dr. Scott said that in the bright anodizing sulphuric acid bath the chlorides must be kept low, and a figure of 1 part per 10,000 in the brightening bath was required, so that deionized water had to be used. In the case of the sealing treatment the chlorides were not so important, but it was important that sulphuric acid from the film should not accumulate, and an optimum *p*H for

the sealing water of about 6 should be aimed at. Below a *p*H of about 5, alumina began to dissolve, forming aluminium, and at a *p*H greater than 7 the aluminium dissolved forming aluminate, so that a *p*H of 6 ought to be maintained.

Whether to seal in boiling water or steam was a matter of choice. The advantage of steam was that no matter how dirty the water the sealing was always done with distilled water. The question of waxing had been raised by Mr. Walker. Sealing, in distilled water or steam, sealed the film and made it impervious; but when it had to be handled, as in pen caps, waxing certainly improved the feel. Whether it was necessary for motor car trim was another matter, but the owner would probably wax it later.

On the question of trichlorethylene *versus* Vienna lime for degreasing or cleaning, Dr. Scott and Mr. Pullen preferred trichlorethylene, but the authors who recommended the use of the bifluoride bath also recommended Vienna lime. Presumably that was used on a polishing mop, in which case there was a degree of pre-polishing.

Mr. Bache had asked what frequency of replenishment was necessary on a 40-hour week basis. Dr. Scott could not answer that question explicitly, but the answer could be based on the analysis of the solution. One advantage of the alkaline solution was that it could be analysed for carbonate and for phosphate. Loss of carbonate was due only to drag-out losses, and loss of phosphate to drag-out losses plus some deposition of aluminium phosphate.

With regard to the tank lining, rubber or p.v.c. could be used as well as lead. The rinse tank need not be similar in capacity to the brightening tank, but merely sufficiently large to contain the sample. Water sprays could be used. A spherical object such as a teapot could often be treated spout upwards and a sufficiently bright finish could be obtained all over. The anode should be given 12 oscillations per minute to give an improved finish.

They did not use nickel acetate, but included it because it was used on the Continent. Their impression was that it was 1-2 per cent and not 10 per cent, and in that case an aluminium tank should be satisfactory for containing it.

Mr. A. W. BRACE in the course of his reply to the discussion said that more needed to be known about the effect of metal composition on the response to phosphoric brightening. The main point was that phosphoric brighteners tended to be maids of all work and give good results on most aluminium alloys, if the right composition and operating conditions were chosen. It was possible to get good brightening in this way, but brightness after anodizing was a function of the film thickness. It would be disastrous if the motor car industry tried to get its bright finishes by using low purity materials with low film thicknesses, because that would quickly bring bright anodized aluminium into disrepute. It was better to start with a material with a little more protection than it needed than to start off on the wrong foot and pay dearly for the experience. There was a considerable difference in the corrosion resistance of lower purity aluminium when anodized compared with the super-purity material.

There seemed to be no doubt from the papers that there were a number of brightening methods which were possible for commercial operation, but he would like to reinforce the plea made by Dr. Hoar and others for a greater understanding of the way in which these processes worked, particularly from the quantitative aspect. Mr. Brace hoped that there would be a greater interest taken in the subject in the aluminium industry and in the metal finishing trade.

Dr. G. E. GARDAM said that the answer to some of the comments which had been made about the suitability of these processes for commercial-purity aluminium was that it was possible to brighten such materials, but to anodize them was extremely difficult. He knew of no method by which it was possible to get an adequately protective film which was at the same time so completely transparent as to preserve the brightness. He would like to make the plea that no attempt should be made to circumvent that difficulty by reducing the thickness and therefore the protectiveness of the anodic film, because if that were done the whole subject would fall into disrepute.

Another very important question which had been raised, and to which he did not entirely know the answer, was the extent to which prepolishing was necessary with the ammonium bifluoride type of process. The authors had described the original ammonium bifluoride process, which produced, by means of considerable attack, a surface which had a certain lack of image clarity, but the process had a very strong smoothing action and would remove light emery scratches. Nevertheless, in production handling might give rise to scratches, and it might be necessary to polish those out.

Since writing the paper, however, modified ammonium bifluoride processes had come to light which would increase the final image clarity and make it possible to get surfaces with reduced rate of attack and with consequently less smoothing action. A little polishing might then be necessary, but a case could be made for very much less polishing before the ammonium bi-

fluoride rather vigorous attack than with some of the so-called electro-brightening processes.

Their production experience was limited to control tests on sheet material and experimental work, but on production tests on sheet material they had done a good deal of work. The material was supplied to them in the shape of flat plates which were in good surface condition, and when brightened their condition was excellent without any polishing whatever. Commercial car trim went through many stages involving tooling operations and so on, at any rate in some cases, and it was impossible to generalize and to say that all the marks could be removed without polishing.

He did not propose to enter deeply into the theoretical questions which had been raised, but lead was an essential catalyst in the process, and the fact that it happened to be an accidental impurity in ammonium bifluoride was perhaps fortunate. They had tried copper, but without success. The super-purity material was produced from an aluminium-copper alloy, and copper was a slight but possible impurity in super-purity aluminium which would build up in the bath.

With regard to the health hazard, ammonium bifluoride-nitric acid solutions were not the best to deal with, but he would prefer to work with them than with phosphoric acid-nitric acid solutions.

Abstract No. 5:

Smoothing of Mild Steel by Barrel Treatment in Oxalic Acid-Hydrogen Peroxide Solution.

By K. Sachs, Ph.D., M. Sc., A.I.M., and M. Odgers.

THIS paper describes a series of experiments made on mild steel to see if it is possible to obtain smooth and chemically polished surfaces at a reduced cost.

The solution used in all these experiments consisted of 2.5 gm. oxalic acid, 1.3 gm. hydrogen peroxide (100 vol.), 0.01 gm. sulphuric acid and made up with distilled water to 100 ml. This solution was discovered by Marshall to have a pronounced smoothing action on steel surfaces. In the solution the steel surface was covered with a film of protective oxide which is periodically dissolved and reformed. This film was particularly thin at asperities in the metal surface and consequently the base metal at the asperities was exposed for a major part of the time cycle allowing the surface projections to be smoothed out and preventing a general attack on the remainder of the surface.

Chemical polishing processes depend on the degree of surface smoothing that can be achieved. Optical reflectivity, however, depended on surface roughness of a fine order and the mechanism of Marshall's solution accounted satisfactorily for the smoothing of the micro-texture and optical brightening of mild steel.

Different initial surface preparations were investigated to assess the practical usefulness of the solution for the polishing of steels, using Talysurf traces recorded at all stages of the experiments as the criterion of surface quality. Mild-steel blocks, ½-in. square and 1 in. long were used throughout the experiments, the sides being ground or shaped to give the required initial finish.

When coarse ground specimens were immersed in a still solution for one hour the secondary roughness was slightly reduced but the primary grinding marks were substantially unaffected. The centre-line average (C.L.A.) dropped from 200 to 190 micro-in. With finely ground surfaces the C.L.A. increased from 4.5 to 7 micro-in. due to a widening of the deep scratches and removal of metal from the shoulders and not an increase in depth or number of scratches.

The results showed that the solution tended to smooth out secondary roughness but with extremely fine surfaces the amplitude of the surface tecture increased slightly.

Another experiment used six specimens, having a different ground finish on each face, which were tumbled in a barrel of the solution. The results showed that the C.L.A. went down in each case after 1-hour's tumbling. The surfaces were a little dull but were brightened by a very short immersion in still solution. They were then tumbled for another hour in the same volume of a fresh solution and given a brightening dip. Except on the coarsest surface this treatment had a significant roughening effect, while the dip in the still solution increased the optical brightness on all surfaces, but all the centre-line averages showed further roughening.

It was apparent from these results that smoothing and roughening could occur in the same solution and that one or the other predominated under different conditions. Also the longer the treatment the duller the resultant surfaces became. From this it appeared that once the solution became stale the polishing ceased and etching, due to the acid, took place.

To test this conclusion some specimens were tumbled twenty times in fresh solutions, each for half an hour. This showed conclusively that brightening and smoothing occurred so long as the solution remained fresh, and also the lowest C.L.A. that could be obtained was about 10 micro-in.

A further test was made to see if it was possible to eliminate surface markings. After eight treat-

ments the scribed line had been virtually eliminated.

Repeated barrelling had been found to affect the shape of the components, sharp corners became radiused and flat surfaces were rounded. However, it was thought that this effect was not inherent in the polishing mechanism and could be kept under control. Nevertheless results did show that there was a tendency to produce convex faces rather than rounded corners. This was thought to be due to the conditions of flow of the solution over the surfaces. Differences in the conditions of flow lead to differences in curvature and detailed study of this effect should make it possible to control the flow in such a way that the gross geometry of the surface remained unaltered.

From all the results collated it was apparent that barrel tumbling achieved a far better degree of smoothing than that which could be obtained by immersion in a still solution. The mean amplitude of the surface roughness corresponded to the centre-line average, and for fine and coarse ground surfaces it was about 10 and 200 micro-in. respectively.

The solution attacked all the surface but was more rapid on projections and slower on depressions and these relatively slight differences in the rate of solution accounted for the smoothing and polishing effect. As the projections diminished in size the extent to which they interfered with the flow of the solution diminished and the rate of smoothing slowed down until the surface was sufficiently smooth for the solution to flow over it undisturbed.

Rough surfaces could be gradually smoothed to a finish of 7 to 10 micro-in. by repeated short treatments in a tumbling barrel containing fresh Marshall's solution. However the higher the ratio of surface area to the volume of the solution the sooner it became stale and then etching occurred. There was no limit to the number of treatments that could be given but the number required depended for a given finish on the roughness of the original surface. The metal was dissolved at a rate of about 0.001 in. per hour, so that dimensional changes had to be allowed for in design.

It was probable that polishing proceeds by a cyclic mechanism involving the alternate formation and solution of a passive film; the number of such cycles per hour and the rate of metal solution at different parts of the surface were functions of the rate of flow, which was higher at projections than depressions in the surface.

Discussion

Dr. W. A. MARSHALL (A.R.E.), opening the discussion, said that the paper raised a number of interesting questions. It was doubtful whether the mechanism postulated by Hickling and Rostron could account solely for the phenomena reported, although some of the effects observed in the tumbling experiments might have been predicted. Hickling had shown that, in the periodic attack which was typical of this process, the amount of steel dissolved per cycle was substantially constant, so that the overall rate of dissolution was proportional to the frequency of periodicity. Any change in physical conditions which, by accelerating diffusion at the steel surface, increased the frequency of periodicity would correspondingly increase the rate of solution. Agitation, heating and the application of a cathodic potential were all known to have this effect; in fact, the rate of attack quoted in the present paper was of the same order as that found in the experiments with which Dr. Marshall had been concerned, with a rotating specimen, to which the authors had referred.

The periodic mechanism upon which micro-smoothing depended took place very near the steel surface (according to Hickling and Rostron, within approximately 0.0015 cm.) so that, even with the slow barrelling described, this very local action might be able to proceed. Indeed, the polishing (*i.e.*, micro-smoothing) of the steel reported was strong evidence that that was so.

The striking macro-smoothing action was evidently due to a very different cause, and there he felt that the solution was probably acting as any other acid-etching medium, suitably restrained, would behave. Dr. J. Edwards had pointed out that all dissolution from a metallic surface resulted theoretically in an overall flattening, provided that no local attack on grain boundaries intervened, and it might well be that in the present experiments such an effect had occurred. It would be of great interest to repeat some of these, using a conventional inhibited acid medium, and to study the macro-effects obtained in the absence of polishing action.

So far as the roughening reported in several of the experiments was concerned, two entirely different causes might be involved. In the work with which Dr. Marshall had been associated, instances had been observed of roughening associated with grain-etching, which sometimes occurred during prolonged treatment of particular specimens in solution capable of the normal brightening action. On the other hand, other specimens had been observed to remain bright and smooth almost indefinitely, and this difference of behaviour was attributed to variation in the original physical state of the steel. Any treatment which tended to refine the grain-size—*e.g.*, cold work or case hardening—appeared to enhance the polishing characteristics of the steel.

A different type of roughening took place when the solution was allowed to become exhausted, and in that connexion a brief reference to the chemistry of the process might be helpful. The iron taken into solution formed with the oxalic acid present a complex ferrioxalate, $H_3Fe(C_2O_4)_3$, in which the iron was combined with 6.75 times its own weight of oxalic acid. This complex was extremely feebly dissociated, and the oxalic acid was thus removed from the sphere or reaction; 25 gm. of oxalic acid were thus associated with 3.7 gm. of iron, and this weight of iron was the maximum which could be held as complex by 1 litre of smoothing solution. Although, as suggested by the authors, polishing would no longer take place upon the exhaustion of the peroxide, it was more usually the removal of oxalic acid by complex formation which determined the effective life of the solution.

When treatment was continued in exhausted solution, the steel ultimately became coated with a visible film of ferrous oxalate, the solution became turbid, and some roughening of the steel occurred. If now the coated specimen was immersed in fresh solution, as in the brightening dip described, the film was rapidly oxidized and dissolved.

It would be agreed, he thought, that some unexplained instances of pitting, particularly on horizontal faces, had occurred, sometimes with steels which were otherwise ideal for brightening, and that very smooth surfaces, for example ball bearings, deteriorated when treated. However, they had achieved results as low as 4.5 microin, starting from ground case-hardened steel of 7 microin texture.

Mr. C. D. S. BRIDGETT (R.E.M.E., London) said that the objection often made to the solution under discussion was that it was uneconomic. It would make the process less costly if there was any possibility of rejuvenating the solution by adding peroxide, or peroxide and oxalic? When he had been studying it in Germany last autumn he had found that he could rejuvenate it, and he had done so three or four times.

The authors used a very small barrel. Would they have had much difficulty if they had used a full-sized barrel?

One point which had puzzled him a little was that Hickling and Rostron found that the film thickness was 0.4 microin, but the present authors gave the limit of smoothing as in the region of 10 microin. If the theory was correct, they should get a little nearer than that.

The authors obtained a surface which differed entirely from a ground surface. What effect on a bearing surface would that have so far as lubrication was concerned? Would it be better or worse?

Mr. R. A. F. HAMMOND (Armament Research Establishment, Woolwich) said that the authors had stated that the applications of the process depended on the surface smoothing attainable. That was true for the applications which they had in mind, but they had themselves referred to other applications in which the polishing action *per se* was not so important, such as its application to inspection and crack detection. There were a few other applications which were quite important but in which the smoothness was not the important criterion, such as de-rusting and salvage work and resistance welding. The last-named was interesting. It had been found that in the resistance welding of mild steel, using a shim of stainless steel for the bond metal, stronger and more reproducible welds resulted from pretreatment of the ground steel surfaces in the A.R.E. solution. This resulted from a much lower and more uniform contact resistance, permitting a higher energy input into the interface during welding.

At the beginning of their discussion of their results the authors had referred to the chamfering effect, the pronounced rounding of corners and edges, which occurred in their experiments. They suggested that in barrelling the rounding was probably not inherent in the polishing mechanism. Mr. Hammond wished to reinforce that suggestion. At the A.R.E. they regarded the maintenance of true form as an important attribute of the process when used normally, *i.e.*, in still solution, and a number of successful applications depended on this. The rounding was a feature of the barrelling application of the process. The authors had accounted for this by the accelerated rate of solution flow over the projecting surfaces, corners, edges and so on, of the articles. He would like to add the suggestion that there might well be a pronounced erosive action at the point of contact between the surfaces of the specimens and the sides of the barrel, and between specimen and specimen, which would probably have a much more significant effect in causing rounding than the mere extra solution flow over the exposed surfaces.

Dr. D. N. LAYTON (Ionic Plating Co. Ltd., Birmingham) suggested that the rounding to which Mr. Hammond had just referred might be due to the actual nature of the barrelling process and not just to the action of the solution.

The authors' theory of the relation of the rate of solution flow over the surface to the smoothing obtained on corners could easily be checked by putting a specimen such as they had used in a long rectangular tank of smoothing solution

and oscillating it up and down the length of the tank, when smoothing and rounding of the corners should be obtained if the authors' theory was correct.

Authors' Reply

Dr. K. SACHS agreed with Mr. Marshall that the Hickling mechanism still operated while smoothing and levelling was going on. It was the Hickling mechanism, which operated more rapidly at the projections than at the depressions of the surface, which was responsible for the levelling. It was conceivable that a cheaper conventional inhibited acid etch could be found to do the levelling, afterwards doing the smoothing off and polishing in Marshall's solution. That was something which they might try.

Roughening by exhausted solution had been described by Mr. Marshall, who seemed to take the view that it was the oxalic acid which was exhausted first and not the hydrogen peroxide. Dr. Sachs had no theoretical comments to make on that, and Mr. Marshall was probably right; but Mr. Bridgett had stated that it was possible to regenerate the exhausted solution slightly by adding more hydrogen peroxide, and it would then continue to polish, which suggested that it was the hydrogen peroxide which was exhausted.

Replying to Mr. Bridgett, Dr. Sachs said that he had already referred to the authors' very limited experience of rejuvenating the solution with hydrogen peroxide. On the effect of the size of the barrel, from first principles he would not expect the use of a larger barrel to make much difference, but experience showed that one was always liable to run into trouble unless one tried these things. With regard to the effect of the 0.4 microin thickness of the film, 0.4 microin was the thickness of the film in any one cycle, and in the course of treatment there were very many cycles, so that the 0.4 was multiplied a number of times.

The authors had no evidence of the effect of the sort of surface with which they were concerned on lubrication problems.

He agreed with everything that Mr. Hammond had said about other uses. They themselves had used it for other purposes. He agreed that the rounding of the surfaces was exclusively due to the use of the barrel, to mechanical erosion. They had tried the experiment of putting a few specimens in a barrel in water—he did not remember whether a wetting reagent had been used —and the effect on the removal of metal from the surfaces had been almost nil.

Dr. Layton referred to the rate of solution at the corners. The authors had carried out an experiment by taking a cylindrical bar, screwing it to a small electric motor and using it as a stirrer, putting it in a beaker of the solution so that the bar went round the solution, but, since it was not completely concentric, it did not move round concentrically but in the form of an oval. On taking it out after 15 minutes or so they found that it had lost its cylindrical shape and become oval, because it had been held rigid in the solution. They had contemplated the use of that as a method of making turbine blades, but decided that it would not be economic.

Abstract No. 6:

The Electrodeposition of Tin-Zinc Alloys from Stannate-Complexone Solutions.

By A. E. Davies, Ph.D., D.I.C., A.R.C.S. and R. M. Angles, A.I.M.†*

THIS paper describes a preliminary investigation in to the electrodeposition of tin-zinc alloy from cyanide-free alkaline solutions containing the trisodium salt of N-hydroxyethylethylenediamine triacetic acid.

In the deposition of tin-zinc from cyanide-stannate solutions there is some evidence that anode solution is affected by the decomposition of cyanide, which takes the form of a brown encrustation on the anodes causing a drop in efficiency. If the bath voltage is increased to offset this, anode deterioration may be aggravated and if parts of the brown layer fall away extreme local attack on the anode may be caused. Although there are measures by which the above effects may be reduced, the need to take these measures, in addition to the other inconveniences common to all cyanide solutions, stimulated the search for alternative processes for depositing tin-zinc alloys, that using N-hydroxyethyl-ethylenediamine triacetic acid giving solutions capable of depositing the alloys.

The solution used was compounded from sodium stannate, sodium hydroxide, zinc carbonate, and the trisodium salt of N-hydroxyethylethylenediamine triacetic acid. The complexing agent was used in the form of a solution containing one grain-molecule per litre of the trisodium salt (the " complexone solution "). Zinc was added by dissolving the zinc carbonate in this solution.

The effect of variations in metal concentration, hydroxide concentration, complexone concentration, temperature and current density on cathode efficiency and deposit composition were studied. Anode efficiency was also investigated. A bath was operated for six months and throughout the test satisfactory deposits were obtained. The anode efficiency (using alloy anodes) declined as the test proceeded and fell sharply at the end of

*Formerly Tin Research Institute
†Tin Research Institute

five months and the test was terminated. A final month's operation was carried out with tin anodes which developed the usual yellow film and dissolved normally. During the test the bath was analysed weekly and the composition of the electrolyte was corrected for caustic-soda and metal content. No additions of complexone were made. At the end of the test the complexone content of the bath was 15 ml. of solution per litre of electrolyte, and 20 per cent of the loss was due to drag-out. It would appear that additions of complexone to the bath as required would maintain anode efficiency at the required level, and these additions would not cost any more than cyanide replacement for similar conditions of operation. The solution gained no iron content in use and the presence of the complexone did not affect the formation and determination of stannite.

The tests have shown that an alkaline bath without cyanide can be operated for tin-zinc deposition without increased cost; and the bath should be particularly useful for automatic plants using tin anodes. Although further development is required the process shows promise, and tin-cadmium alloys have been deposited in the laboratory from similar solutions.

Discussion

Dr. D. N. LAYTON (Ionic Plating Co. Ltd., Birmingham), said that the authors had found on the long-term trial that there was no pick-up of iron in the solution when used for three months in a bare steel tank. That was all right under laboratory conditions, but in the average plating works the steam coils in the tank were usually anodic from electrical leakage. Had the authors obtained any results on the amount of iron taken up by the solution if the steel was made anodic? He pointed out that there were various de-rusters which used E.D.T.A. and related chemicals.

The paper described the use of alloy anodes, but it was possible to use separate tin and zinc metal anodes in the normal alloy-depositing solution, and it might be required to do the same in the authors' solution. If zinc anodes were to be employed, it was convenient to use zinc balls suspended in a steel cage.

The authors mentioned that the solution was made up using zinc carbonate and the complexone added separately. Later, in reporting the results of the long trial, they said that the zinc content was brought up to optimum conditions by adding sodium zincate. Was there any reason for that difference of operation, and why was sodium zincate not used in the first place? They had indicated that the zinc content of the deposit increased with the zinc concentration in the solution, but it was also reported that it increased with increasing complexone concentration, which was not what would be expected from experience of cyanide solutions, where if the complexing agent concentration was increased the rate of deposition of the metal usually decreased. The cathode efficiency also rose with increasing complexone concentration, which seemed at first sight curious. Moreover the anode efficiency rose rapidly with increasing complexone concentration. Did this mean increased dissolution of zinc? The anode and cathode efficiencies had presumably been measured on quite short periods of deposition, and it would be interesting to find what effect over a long period this increased anode efficiency had on the actual composition of the solution. After a long period of continuous electrolysis, did the balance of metals in the solution go up?

The average anode efficiency was reported as 68 per cent and the average cathode efficiency as 70 per cent, so that they were about equal. The amount of tin added, 18 gm. per litre, represented 61 per cent of the original tin concentration in the solution. The complexone loss was equal to 70 per cent of the original concentration, giving discrepancy of 9 per cent. The anode and cathode effieciencies being roughly equal, the loss of tin must presumably be drag-out loss, and therefore the loss of complexone by drag-out should be of the same order *viz*, about 60 per cent; but on page 7 the authors said "It was estimated that at least 20 per cent of the loss of complexone was attributable to drag-out." What was the justification for that estimate of drag-out loss when it appeared that at least 60 per cent of the complexone loss must be due to drag-out?

Dr. J. K. AIKEN (Geigy Co.), in a written contribution read by Dr. J. Edwards, reported that the authors' remarks on poor anode efficiency in tin-zinc plating from an E.D.T.A. bath, possibly due to anode filming with free E.D.T.A., applied also to other metals which could otherwise be satisfactorily plated from an alkaline solution of E.D.T.A. complex, for example, lead, copper and iron. Moreover, in these cases also the disadvantage could be overcome by the use of the hydroxyethyl substituted chelating agent. A more detailed statement on this work, on some aspects of which a patent application had been made, was in preparation.

In British Patent 737,713 reference was made to plating of lead alloys from an E.D.T.A. solution where adequate anode corrosion was ensured by the incorporation of a hydroxy-acid such as tartaric acid. The key to the problem of

the successful use of complexones in electrodeposition seemed to be the combination of hydroxyl groups with powerful chelating activity, and it was logical to combine these in one molecule.

Mr. R. M. ANGLES, replying to the discussion, said that there was no need to reply to Mr. Aiken's question, because he had answered it himself by saying that the complexone N-hydroxyethyl-ethylenediamine triacetic acid had given satisfactory results.

In reply to Dr. Layton, the actual time for which the bath had been run, in an attempt to run it to exhaustion, was six months, and during that time there was no iron pick-up by the solution. It would be interesting, however, to investigate the effect of electrolysis. The six-months' test had been carried out in a steel tank, and, although it did not have steam coils in it, it was possible to have the tank bipolar; however, ordinary analysis did not show any iron in the solution after the six months.

The zinc in the solution was extremely small, and it seemed to be much easier to add it as a complex with the complexone solution rather than to use zinc anodes. Tin anodes worked very well even in a solution of extremely low complexone concentration, and the reason for using zinc carbonate orginally and changing to sodium zincate was that it was much easier to make a solution from the zinc carbonate. Sodium zincate had been used because in the six-months' trial it was necessary to avoid complexone additions to the solution. Account had to be taken of the fact that a considerable amount of caustic soda was used to form the sodium zincate, and due allowance had to be made for that; when the bath was made up, allowance must be made for the caustic soda in the zincate.

So far as the balance of the solution was concerned, it conveniently fitted in with the weekly analysis, so that over the period of six months it appeared to be balancing. Whether or not during the weekly periods the bath got slightly out of balance Mr. Angles was not sure, and a good deal more work had to be done before it was known whether the bath was a practical proposition or not.

He regretted the slight discrepancy that Dr. Layton mentioned; it was quite possible that a slight error in the calculation of the final complexone had been made due to the methods of analysis which he had used.

Abstract No. 7:

A Preliminary Investigation of the Formation of Cracks in Hard Chromium Electrodeposits and the Evolution of Hydrogen During Deposition.

By C. P. Brittain, B.A. and G. C. Smith, M.A.

THIS paper describes a series of experiments involving the electrodeposition of chromium from aqueous solutions containing 50 gm. per litre chromic anhydride and 0.5 gm. per litre sulphuric acid. These solutions are relatively transparent and thus it was possible to examine the cathode on which chromium was being deposited.

A special microscope was used to examine the cathode in the chromium-deposition cell which compensated for aberrations introduced when viewing through a medium other than air. The cell was also specially constructed to allow the cathode to be viewed through a glass cover-slip in its side. The cathode was a 0.25 cm. diameter 0.4 per cent carbon-steel cylinder 6.5 cm. long mounted in a methyl methacrylate holder, while the anode was a 0.4 cm. wide lead strip terminating just above the level of the cathode. The temperature was kept constant at 45°C. and the current density was 20 amp. per sq. dm.

To start the experiment the microscope was focussed on the surface of the cathode before the current was switched on and it was possible to observe the build-up of the chromium deposit from the basis metal to the stage at which material was being deposited on an existing thick layer of chromium.

When an e.m.f. was first applied gas bubbles were liberated from the cathode but as the chromium deposit built up they decreased until the preferred centres of nucleation became extinct. In three minutes the visible evolution of gas was suppressed.

After six-minute's deposition, which corresponded to a chromium thickness of 0.0002 cm., cracks in the deposit occurred. This formation did not take place continuously but appeared abruptly every two or three minutes. With the formation of these cracks large quantities of gas bubbles were liberated. The evolution lasted for about thirty seconds and then died away rapidly until new cracks occurred two or three minutes later. The cracks did not take place over the complete surface of the deposit but only over discrete areas and once they were formed they became rapidly less distinct as further chromium was deposited and were no longer clearly visible after ten minutes. Cracks sealed in this manner did not reappear during any subsequent cracking.

The complete absence of visible gas bubbles from the cathode surface during the major part of the process and the periodic appearance of newly-formed cracks were phenomena previously unsuspected.

The absence of visible gas bubbles might have been due to the absence of nuclei on which they could form or to the complete wetting of the cathode surface, in both cases the liberated hydrogen would pass into solution in the electrolyte. It was also possible that the hydrogen released might have been involved in a chemical reaction with a component of the plating solution or that the amount of hydrogen produced was so small and the major part of the cathodic reaction involved the partial reduction of hexavalent chromium ions which were reoxidized at the anode.

One explanation was thought to be that when a crack was formed it contained a vacuum in communication with the electrolyte in contact with the cathode. If the electrolyte was supersaturated with hydrogen, that element would then pass out of solution or, diffusion of codeposited atomic hydrogen would build up to a high pressure and then rupture the chromium and release the gas. However, when the plating-cell current was switched off during a burst of bubbles, the burst ceased immediately. When the current was switched on again the burst recommenced, apparently from the stage at which it was interrupted.

It is probable that the evolution of gas is an electrolytic process. It was thought that the gas was generated in the interior of the crack because the peaks of high current density would be much reduced if the edges of the cracks had been rounded off. In addition it was suggested that the crack was sealed off by virtue of the concentrations of current along its edges. After the formation of the crack these concentrations were such that chromium built up rapidly across the crack and also in a direction normal to the surface of the deposit, thus sealing off the crack and also producing a disturbance in the covering layer of chromium. As the crack sealed over, gas at high pressure might be trapped in it and would account for a proportion of the hydrogen content of the specimen. This gas would escape rapidly when the specimen was removed from the bath.

Arising from the experiments it was thought that a relationship existed between the cracking of the deposit, the periodic evolution of gas bubbles and the banded structure. It was difficult to identify cause and effect, but the logical process would seem to require an increase in internal contractile stress leading to cracking, followed by the evolution of gas from one of the cracks.

Cracking would result in a decrease in internal stress which might be associated with the nucleation of a fresh structure and therefore lead to striations. Alternatively the latter might result from the violent periodic stirring of the solution in the region of the cathode occasioned by the release of gas bubbles from the cracks.

Discussion

Mr. R. A. F. HAMMOND (Armament Research Establishment, Woolwich), opening the discussion, said that the authors differentiated between the initial period of gassing, lasting 3 minutes, when deposition commenced on a new steel surface, and the periodic local bursts of gassing which appeared subsequently. The initial gassing might be accounted for either by assuming that the hydrogen overvoltage on an incompletely covered steel surface was lower than on a continuous chromium surface or, what was less likely, by the time required to establish the cathode film for which purpose however, a period of 3 minutes seemed unduly long. In that connexion, he would like to ask whether the authors had observed if any gassing occurred on resumption of deposition when the current was broken during the quiescent phase.

It had been shown that hydrogen evolution took place periodically at the site of the uniform cracks, and this effect appeared to operate even on a macro scale. The question then arose of whether the whole or a considerable proportion of the low metal efficiency characteristic of chromium deposition could be accounted for on the supposition that the metal efficiency was approaching 100 per cent, during the quiescent phase and zero during the gassing phase. However it could easily be calculated from the figures quoted by the authors that the gas evolved periodically at the site of cracks accounted for only a small proportion of the low efficiency.

Was it possible that superimposed on the periodic gassing at freshly-formed cracks there was a steady, general and continuous evolution of hydrogen not observed by the authors because it was used in the reduction of hexavalent chromium? It might be possible to arrange a simple experiment which would collect and measure the hydrogen evolved from the cathode and in addition determine analytically the amount of cathodic reduction of chromic acid. This could be accomplished by having the cathode in a separate cell, to avoid reoxidation at the anode. The occluded hydrogen could be accounted for by analysis or by reference to published data, and the absorption of hydrogen prevented by using a suitable metal for the cathode, *e.g.*, copper.

The second point of major interest in the paper concerned the explanation of why bursts of hydrogen bubbles occured at the site of newly-formed cracks. The authors were, probably right in concluding that the gassing was an electrochemical phenomenon. Mr. Hammond was not

fully satisfied, however, with the assumption that gassing after a break in deposition precluded the possibility that the hydrogen came out of solution in the electrolyte. The catholyte might become saturated with hydrogen almost instantaneously after switching on the current and the localized evolution might then be accounted for by the sharp edges of the newly-formed cracks acting as nuclei.

There were, however, two further possibilities. One was that the hydrogen overvoltage might be much reduced on the sharp edges of a freshly-cracked surface, which would account for a sudden burst of gassing when cracking took place, and the second was that the cathode potential, and therefore the tendency for hydrogen ions to discharge, might be affected by the internal stress in the chromium deposit. It was well known that the electrode potential of a metal was affected by internal stress in the metal, and even small displacements of potential might be important in the threshold conditions which appeared to obtain during chromium deposition.

Mr. H. FRY (B.N.F.M.R.A.), in a written contribution read by Dr. J. Edwards, said that it was generally held that there was a layer near the cathode which had a lower *p*H value than the bulk of the solution, and which contained a relatively higher proportion of reduced chromium compounds. Due to the presence of lower valency compounds, this layer should have a darker colour than the bulk of the solution. The layer could sometimes be seen when a cathode was withdrawn from a chromium-plating bath, and it had been described and investigated by Weiner. Mr. Fry wondered whether this layer had been observed by the authors in the course of their experiments.

The authors had shown that old cracks were not closed over until at least four new sets of cracks had appeared. It was therefore difficult to see how the closing of newly-formed cracks could be responsible for the cessation of hydrogen evolution after very short periods of time, corresponding to a thickness which was only a small fraction of the distance apparently required to close a crack.

This difficulty would be largely removed if it was assumed that periodic changes in the composition of the cathode layer were responsible for the periodic evolution of hydrogen as well as for cracking. The fact that hydrogen was preferentially evolved from the cracks might well be simply because the cracks represented discontinuities which nucleated gas bubbles just as, apparently, did the edge of the cathode.

If this assumption were accepted, then it was relatively easy to see why there should be increased hydrogen evolution consequent upon a brief reversal of the current. It was suggested that this might be due to a decrease in the *p*H of the electrode film which occurred while the electrode was anodic.

Mr. J. W. OSWALD (Fescol Ltd., London), said that Ogburn and Brenner using radioactive chromium had shown conclusively that chromium was deposited directly from the hexavalent state and not through a series of reductions. Brittain and Smith seemed to show that deposition occurred mainly during periods when no hydrogen was visible, and it seemed possible that during such periods chromic acid was being directly reduced to chromium at the cathode surface. After a time the cathode layer would become depleted of chromium, and hydrogen would then begin to evolve and would be evolved until the layer was re-established with chromic acid, and then the hydrogen evolution would stop and a further period of reduction would take place. The fact that bubble bursts recurred after the current had been switched off might simply be due to the fact that the chromium surface required activation by hydrogen before further deposition could take place. It would be of interest to know whether, if the current was interrupted during a quiescent period, that quiescent period continued on the resumption of current or was preceded by a burst of bubbles. He wondered also whether this periodic function of the deposition of chromium would also take place using so-called crack-free chromium solutions.

Authors' Reply

Mr. C. P. BRITTAIN, in reply, said he thought that Mr. Hammond's suggestion of low hydrogen overvoltage on steel as being responsible for the initial burst of bubbles was probably correct. What happened when the current was broken during the quiescent stage and then recommenced was that the quiescent stage continued until the next bubble burst was due. If the quiescent stage had been allowed to progress for one minute after a bubble burst and the current was then switched off, when the current was switched on again it would be necessary to wait for approximately another minute for the next burst of bubbles.

The suggestion that they should measure the amount of hydrogen evolved was an extremely good one. They had hoped to do it but had not had time. It should be fairly straightforward and it was surprising that it had not been done before.

Mr. Hammond had also suggested that bubbles

(Continued in page 150)

SOLUTION CERAMICS

A New Temperature-Resistant Surface-Coating Technique

by T. A. DICKINSON

"SOLUTION ceramics" is a term that has been coined to denote a series of adherent, homogeneous mixtures of oxides which can be used as coatings on a variety of materials whose temperature resistance would not permit the deposition and fusion of porcelain enamels and other more or less conventional ceramic finishing dispersions on their surfaces.

Originated by the Armour Research Foundation of the Illinois Institute of Technology, they are currently being developed for commercial applications by The Titanium Alloy Manufacturing Division of the National Lead Company, New York.

They comprise either nitrate solutions or ammonium zirconyl carbonate liquors containing additions of ammonium salts and are applied with spraying equipment and thermally decomposed on deposition surfaces preheated to temperatures of about 500 to 600°F. (260 to 315°C.).

Results obtained with a typical group of aqueous nitrate solutions, which were mixed without precipitation and then sprayed on freshly-sandblasted mild steel plates (each preheated to 600°F. (315°C.)), are shown in Table I. Here it should be observed that the homogeneous colours of the coatings were different from those of the component oxides, probably due to the fact that the deposited oxides had compositions different from those in the starting solutions.

Where complex nitrate coatings were deposited on glass microscope slides, and the slides were softened slightly by heating at 1250°F. (678°C.) for 30 minutes, results indicated in Table II were obtained. Colour changes noted after firing were probably due to crystal growth, since no evidence

TABLE I
Examples of Complex Coatings From Aqueous Nitrate Solutions

Solution Composition* Parts by Volume	Apparent Colour of Coating	Remarks
50 Chromium-nitrate Solution 50 Aluminium-nitrate Solution	Brown	Common remarks are:
50 Aluminium-nitrate Solution 50 Cerous-nitrate Solution	Yellow-green	Coatings deposit readily on steel plates held near 600°F.
80 Cerous-nitrate Solution 20 Chromium-nitrate Solution	Brown	Colours are changed somewhat if application temperature is lowered to 500°F.
50 Aluminium-nitrate Solution 50 Cobaltous-nitrate Solution	Bluish-Black	
50 Aluminium-nitrate Solution 50 Nickelous-nitrate Solution	Bluish-Black	Deposits are insoluble in water, resistant to thermal shock and appear to be densely packed structures.
50 Zirconyl-nitrate Solution 50 Chromium-nitrate Solution	Greyish-Brown	
90 Zirconyl-nitrate Solution 10 Chromium-nitrate Solution	Yellow-green	
50 Aluminium-nitrate Solution 10 Chromium-nitrate Solution 10 Nickelous-nitrate Solution 10 Cobaltous-nitrate Solution 10 Cerous-Nitrate Solution 10 Lanthanum-nitrate Solution	Metallic-Blue	

*Chromium-nitrate Solution —10% $Cr(NO_3)_3 .9H_2O$ by weight
Aluminium-nitrate Solution —25% $Al_2(NO_3)_3 .9H_2O$ „ „
Cerous-nitrate Solution —20% $Ce(NO_3)_3 .6H_2O$ „ „
Cobaltous-nitrate Solution —15% $Co(NO_3)_2 .6H_2O$ „ „
Nickelous-nitrate Solution —15% $Ni(NO_3)_2 .6H_2O$ „ „
Zirconyl-nitrate Solution —10% $ZrO(NO_3)_2 .6H_2O$ „ „
Lanthanum-nitrate Solution —10% $La(NO_3)_3 .6H_2O$ „ „

TABLE II
Heat-treated Complex Coatings
Coatings deposited on glass slides and fired at 1250°F. for 30 minutes.

Solution Composition* Parts by Volume	Colour Before Firing	Colour After Firing
50 Aluminium-nitrate Solution 50 Chromium-nitrate Solution	Opaque-Brown	Opaque Green
90 Aluminium-nitrate Solution 10 Chromium-nitrate Solution	Light Opaque Yellow	Opaque White
50 Aluminium-nitrate Solution 50 Cerous-nitrate Solution	Opaque White	Semi-transparent White
50 Copper-nitrate Solution 50 Nickelous-nitrate Solution	Opaque Black	Transparent Brown

*Aluminium-nitrate Solution —25% $Al_2(NO_3)_3 .9H_2O$ by weight
Chromium-nitrate Solution —10% $Cr(NO_3)_3 .9H_2O$ „ „
Cerous-nitrate Solution —20% $Ce(NO_3)_3 .6H_2O$ „ „
Copper-nitrate Solution —10% $Cu(NO_3)_2 .6H_2O$ „ „
Nickelous-nitrate Solution —15% $Ni(NO_3)_2 .6H_2O$ „ „

of chemical reaction between the component oxides and no loss of adherence could be detected. Two of the coatings attained a degree of transparency as a result of their solubility in the softened glass.

Table III shows a wide range of colourful coatings that have been obtained by spraying solutions comprising stepwise proportions of aluminium nitrate and chromium nitrate on mild-steel plates at 600°F. (315°C.). All of these coatings had good adherence, low porosity, and excellent thermal shock resistance; underwent colour changes when heated for a few minutes at 1200°F. (648°C.).

The only salt additives known to be suitable for use in solution ceramics based on ammonium zirconyl carbonate liquor are ammonium chromate, ammonium molybdate, and ammonium vanadate. Table IV indicates results that have been obtained after pneumatically spraying such compositions on steel plates preheated to 500°F. (260°C.).

Like the nitrate solutions, combinations of ammonium chromate and ammonium zirconyl carbonate solutions appear to be stable in all proportions.

Ammonium molybdate, on the other hand, reacts with ammonium zirconyl carbonate liquor. This reaction becomes more noticeable and rapid as the molybdate concentration is increased, and precipitation occurs generally within 10 minutes after a 50-50 solution mixture is prepared.

Only small amounts of ammonium vanadate can be added to ammonium zirconyl carbonate liquor, due to the former's low water solubility (which is limited to about a 2 per cent solution by weight).

Sodium silicate (water glass) and water-soluble silicone additives have also been used in ammonium zirconyl carbonate solutions. The most stable solutions were obtained by first diluting the ammonium zirconyl carbonate liquor as received with two parts of water, and then dropwise adding the silicone or silicate in amounts not exceeding 1 per cent by weight of the total solution. Stirring

TABLE III
Chromia-Alumina Coatings
Deposited on Mild-steel Plates at 600°F.

Solution Composition* Parts by Volume		Apparent Colour	Reflectometer Readings		
Aluminium-nitrate Solution	Chromium-nitrate Solution		Green	Blue	Amber
100	0	White	64	65	64
95	5	Pale greenish-yellow	58	31	60
90	10	Chartreuse	51	24	54
75	25	Yellow-green	36	11	43
50	50	Brown	18	7	22
25	75	Dark-Brown	12	10	13
10	90	Black	9	8	9
0	100	Black	6	6	6

*Aluminium-nitrate Solution —25% $Al_2(NO_3)_3 .9H_2O$ by weight
Chromium-nitrate Solution —10% $Cr(NO_3)_3 .9H_2O$ by weight

TABLE IV
Complex Solutions with Ammonium-Zirconyl-Carbonate

Solution Composition* Parts by Volume	Colour of Coatings	Remarks
50 Diluted AZC Liquor 50 Ammonium-chromate Solution	Dark Grey	Coatings appear to be uniformly adherent, water insoluble, and resistant to thermal shock.
90 Diluted AZC Liquor 10 Ammonium-chromate Solution	Greyish-White	
50 Diluted AZC Liquor 50 Ammonium-molybdate Solution	Light Pink	
90 Diluted AZC Liquor 10 Ammonium-molybdate Solution	Essentially White	
33.3 Concentrated AZC Liquor 67.7 Ammonium-vanadate Solution	Pale Yellow	

*Diluted AZC Liquor —Ammonium-Zirconyl-Carbonate Solution 4% ZrO_2 by weight
Concentrated AZC Liquor — " " " " 12% ZrO_2 " "
Ammonium-chromate Solution —10% $(NH_4)_2 CrO_4$ " "
Ammonium-molybdate Solution —10% $(NH_4)_6 Mo_7O_{24}.4H_2O$ " "
Ammonium-vanadate Solution —2% NH_4VO_3 " "

facilitated dispersion.

Zirconia coatings were deposited readily when solutions of the latter type were air sprayed on to heated steel plates, and the additives seemed to act as binders which imparted abrasion resistance. When the coatings were heated and quenched, however, small pinholes appeared, probably due to the thermal instability of the silicate and silicone additives.

As might be expected, deposition surfaces for solution ceramics must be free from rust, scale, and especially grease. If the surfaces are substantial, such foreign matter can be satisfactorily removed by sandblasting; or where grease is deeply embedded, by burning and then sandblasting. Chemical cleaning methods of the types indicated in Table V are preferable where sandblasting might cause damage.

Chromate and phosphate films are generally considered desirable on deposition surfaces that have not been sandblasted, because they tend to facilitate the adhesion of solution ceramic coatings.

Satisfactory chromate films have been deposited on degreased aluminium sheets in a solution comprising 4 per cent sodium hydroxide, 20 per cent potassium chromate, and 76 per cent water by weight. Materials were soaked for five minutes

TABLE V
Caustic and Acid Treatments of Metal Surfaces

Type of Metal	Cleaning Operation	Remarks
Mild Steel	Soak in 6% H_2SO_4 and rinse in water.	Grease film only mildly attacked by acid.
Mild Steel	Soak in 20% NaOH and rinse.	Caustic film left after thorough water rinse. Alkali produces blisters in coating.
Mild Steel	Soak in 20% NaOH, then in 6% H_2SO_4 and rinse with water.	Some etching of surface obtained. Grease spots still present.
Mild Steel	Scrub with soap, neutralize with 6% H_2SO_4, and rinse with water.	Results not as good as with foregoing treatment.
Mild Steel	Scrub with 20% NaOH, neutralize with 6% H_2SO_4, and rinse thoroughly.	Surface can be coated almost as well as when sandblasted.
Mild Steel	Scrub with 10% Tri-sodium phosphate, neutralize with 6% H_2SO_4 and rinse.	Tri-sodium phosphate not as effective as caustic soda.
Stainless Steel	Scrub with 20% NaOH, neutralize in 6% H_2SO_4, and rinse.	Appears to be more effective than the other treatments listed for mild steel.
Aluminium	Dip for a few seconds in 20% NaOH, soak in 6% H_2SO_4 and rinse.	Caustic reacts vigorously to produce deep etching of surface. This treatment can possibly be substituted for sandblasting.

in this bath, which was maintained at 50°C. Then after being rinsed and dried, they were annealed for five minutes at 975°F.

Similarly, degreased steel materials have been readied for solution ceramic finishing by means of a Parkerizing treatment which involved their immersion for ten minutes in a boiling bath consisting of 5 gm. of zinc, 5 gm. of manganese oxide (MnO_2), 18 ml. phosphoric acid (85 per cent), and 750 ml. water.

As already indicated, excellent results have been obtained where solution ceramics were deposited on heated surfaces in a normal, oxidizing atmosphere. However, the potentialities of controlled atmosphere finishing have been investigated by the Armour Research Foundation the results being as follows:—

" The apparatus used in this study is a gas-tight box, 2½ ft. × 1 ft. × 1 ft., constructed of ⅛ in. steel with welded sides and bottom and a flanged, bolted top. This shell was portioned into two 30 inch sections to provide a furnace chamber and an area to contain and operate spray equipment. Appropriate connexions were installed to admit and exhaust protective gases. (The apparatus was assembled as shown in Fig. 1.).

" The furnace chamber was lined with insulating brick and heated with three 475 watt elements connected in parallel to a variable transformer. Temperatures were recorded using a thermocouple inserted through a gas-tight seal in the furnace wall. The heating zone is separated from the working area by a hinged transite door.

" An access door and ¼-inch plate-glass windows were incorporated in the steel walls of the working zone. Two 4-inch diameter flanged holes were provided also. When working with protective atmospheres, these openings were sealed with rubber gloves. Enclosed spray equipment and samples could thereby be handled. Reduced pressure operation required that the gloves be replaced with rubber plugs. Through one plug was inserted a flexible cable for manoeuvring the furnace door. The other plug was fitted on the shaft of an extension-type spray gun controlled by outside operation.

" Helium gas was used for a protective atmosphere. The gas was metered, with a combination pressure regulator and flow meter, through the furnace and spray chamber. A slight positive pressure was maintained on the unit. A second tank was connected to the spray equipment.

" The preparation of zirconia coatings in a helium atmosphere was tried first. Furnace temperature was set at 500°F. (260°C.). The unit was then flushed with helium while sample plates and the spray gun were placed inside. After the access door was closed, gas flow was reduced to 3 cu. ft. per hour. Each plate was mounted on a pedestal in the furnace and heated for at least ten minutes before spraying was started.

" Sandblasted samples of steel, stainless steel, aluminium and copper were coated with zirconia. Good quality coatings were obtained (considering the awkward manoeuvring necessary in a confined space). Thermal decomposition of atomized ammonium zirconyl carbonate appears to progress identically in helium and under atmospheric conditions. No noticeable difference in size or structure of the coating particles could be detected by microscopic examination.

" It is important to note how well copper was coated in a non-oxidizing atmosphere. Normally, when this metal is heated in air, a poorly adherent oxide scale is formed rapidly and prevents bonding of the zirconia.

" The furnace temperature was raised to 600°F.

TABLE VI
Combinations of Solution and Flame Ceramic Coatings

Coating Composition	Remarks
¾ mil. of solution ceramic zirconia overcoated with 3 mils. of flame ceramic 2 L Z 2 L Z — 98% Zirconia 65 mesh, by weight. 2% Lithium aluminate by weight.	Coating of good appearance obtained. The flame ceramic overlayer is somewhat softer than if it is applied directly over bare steel.
Solution Ceramic chromia film overcoated with 2 mils. of flame ceramic 2 L Z.	Poor bonding of the flame ceramic zirconia is obtained over the chromia film. Overlayer tends to blister.
1 mil. of solution ceramic zirconia overcoated with 3 mils. of flame ceramic 3 L A. 3 L A — 97% by weight of 500 mesh acid washed alundum. 3% by weight of Lithium aluminate.	Considerable skill required to deposit a satisfactory overlayer. Alumina overcoat is softer and less adherent than on bare steel.
Solution ceramic chromia film over-coated with 2 mils. of flame ceramic 3 L A.	Very difficult to prevent blisters from forming in alumina coating. Poor bonding to chromia film obtained.

(315°C.) to deposit coatings of chromium oxide, alumina, nickel oxide, and cobalt oxide by atomization of the respective nitrate solutions. The controlled atmosphere produced no outstanding changes in the coatings or in the process except that much improved deposits were obtained on copper. The decomposition products of the nitrates are, of course, oxidizing agents.

" Attempts were then made to deposit coatings at lower temperatures by using a reduced pressure on the unit. It was soon discovered that constant negative pressures could not be maintained. This is due to the positive pressure introduced with the atomized solution and to the fact that the available vacuum pump was incapable of balancing the inlet pressure. To compensate for this, attempts were made to operate the spray gun without atomizing gas. When the fluid needle was opened, however, the vacuum simply pulled in a jet of liquid rather than a spray.

" Zirconia coatings were deposited on steel plates even though vacuum readings fluctuated between 25 and 5 inches of mercury. Best results were obtained in the normally used temperature range of 400 to 500°F. (204 to 260°C.). Temperatures even slightly below 400°F. produced blistered coatings."

Because they comprise networks of fine particles with poor abrasion resistance, solution ceramic coatings should be especially useful as ground or primer coatings for flame-sprayed ceramic finishes —which are relatively porous and resistant to abrasion. However, results in this connexion have not been too encouraging, as indicated by an Armour report which reads:—

" Solution ceramic zirconia and chromia were deposited on sandblasted plates of $\frac{1}{8}$ in. thick mild steel. These films were overcoated with flame-sprayed zirconia and alumina. (*See* Table VI for details.).

" It was difficult to produce cover coats free of blisters. Better results were obtained over zirconia precoats than on chromia. Flame ceramic coatings applied directly to bare steel appear to have greater adherence and abrasion resistance than those deposited over intermediate solution ceramic films.

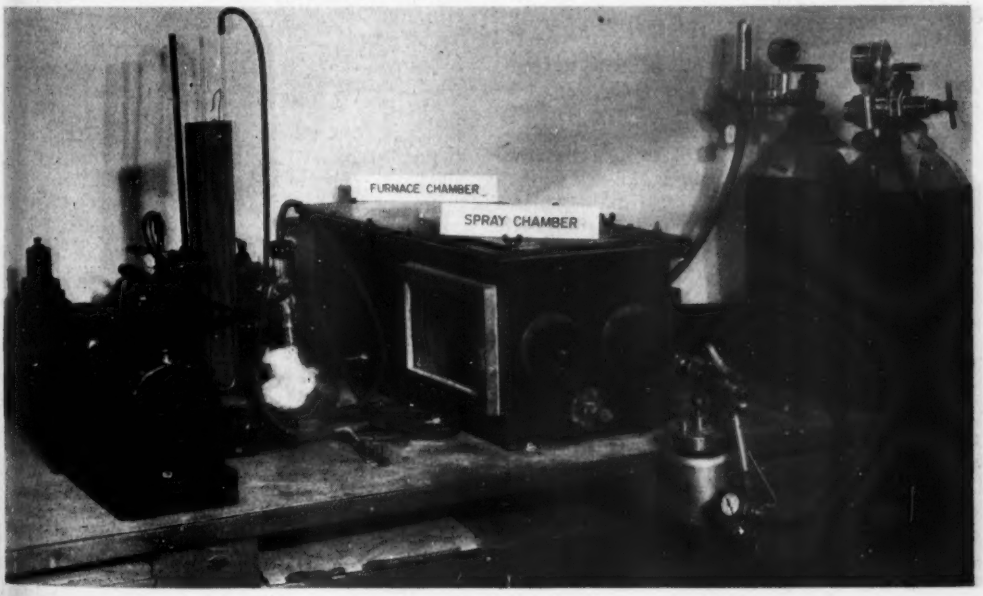
" When the combination coatings were heated to a dull red and quenched, the flame ceramic overlayer usually blistered. The solution ceramic coating remained firmly bonded to the base stock.

" The purpose of these duplex coatings was to utilize the smaller median pore size of the solution ceramic to inhibit wetting of the substrate metal by molten aluminium and the like; flame ceramic alumina over solution ceramic zirconia was found to confer longer life to steel thermocouple tubes in aluminium melting pots than either coating alone."

Lack of abrasion resistance should not be a serious handicap for solution ceramics, regardless

(*Continued in page 150*)

Fig. 1.—Apparatus used by the Armour Research Foundation for spraying solution ceramic coatings onto metal surfaces pre-heated to 400-500°F. in which the whole operation is carried out in an inert atmosphere of helium gas.



INSTITUTE OF VITREOUS ENAMELLERS

Summer School

A SUMMER School arranged by the Institute of Vitreous Enamellers will be held at Ashorne Hill, near Leamington Spa, from June 1 to June 3. A works visit to Cannon Industries Ltd. has been arranged, and for this visit delegates will meet at the Victoria Hotel, Wolverhampton, on June 1, at noon, from where they will proceed to the works by motor coach. Delegates will depart for Ashorne Hill after the works visit. The total cost of attendance at the School is £6 per person and further details may be obtained from the secretary of the Institute at Ripley, near Derby.

Programme

FRIDAY, JUNE 1

1.00 p.m. Assemble Victoria Hotel, Wolverhampton for lunch.
2.00 p.m. Depart for works visit to Cannon Industries Ltd.
5.00 p.m. Depart for Ashorne Hill.
6.30 p.m. Delegates assemble for registration, etc.
7.00 p.m. Dinner.
8.00 p.m. *1st Session:* Discusion on works visit.

SATURDAY, JUNE 2

8.00 a.m. Breakfast.
9.00 a.m. *2nd Session:* "Shot blasting of cast iron for vitreous enamelling," by T. O. G. Wilkes.
10.30 a.m. *3rd Session:* "Furnaces—types, operation and maintenance," by J. A. Swain.
11.45 a.m. *4th Session:* "Dry-process enamelling," by J. Fyfe.
1.00 p.m. Luncheon.
2.00 p.m. *5th Session:* "Preparation of sheet iron for subsequent vitreous enamelling," by H. Symonds.
3.00 p.m. *6th Session:* "Suspension of wet ground enamels," by Dr. German or Dr. Ratcliffe.
4.30 p.m. *7th Session:* "Pyrometers—their construction and care," by L. Neall.
7.00 p.m. Dinner.
8.00 p.m. Address by the chairman.

SUNDAY, JUNE 3

8.00 a.m. Breakfast.

Solution Ceramics

(*Continued from page 149*)

of whether they can be used in conjunction with flame-sprayed materials, since low abrasion resistance is a characteristic of many important inorganic materials—glass, for example. It is not possible, however, truly to evaluate the new coating materials.

In the absence of exhaustive physical test data and applicational experience, it seems fairly safe to say that solution ceramics will find many applications where purely artistic or decorative effects are required because they can be compounded for an almost unlimited variety of colours and applied without great difficulty.

If they compare as favourably as they apparently do with older ceramic coatings, they should further find many functional applications—for example, in the manufacture of kitchenware and plumbing fixtures. And they should have the notable advantage of enabling manufacturers of light or nonferrous metal products to enter fields long monopolized by ferrous metal fabricators. Further, they may greatly reduce the cost of applying ceramic finishes to ferrous materials without incurring a parallel sacrifice of quality.

Of particular interest should be future reports on the thermal shock resistance of solution ceramics; for in this respect, at least, they now appear to have a great advantage over all other non-metallic coating materials.

I.M.F. Annual Conference

(*Continued from page 144*)

might be nucleated on the sharp edges of the cracks. The authors could refute that, because when the specimen was made anodic the sharp edges were destroyed completely, but the bubbles appeared just the same and continued for a much longer period than before.

The effect of internal stress on hydrogen overpotential was a very good suggestion.

Mr. Fry had asked whether they had any evidence of a visible layer on the cathode. The answer was that they had not, but that did not mean that there was not one; it was simply that their technique would not show it if there were.

The time taken to close the crack was of the order of 12 min., as Mr. Fry had suggested. The evolution of gas, however, might be expected to cease before that period, because presumably the crack sealed over, as chromium was deposited on the edges and the current density in the crack would quickly fall to a negligible value.

It was improbable that the cathode surface was reactivated when the current was switched on again, because the bubbles seemed to come from the cracks only and not from all over the cathode surface. If it were a question of reactivating the cathode surface the bubbles would presumably appear from all over the cathode surface, but they seemed to be associated with the cracks and nothing else.

An Investigation into the VISCOSITY of ENAMELS

By
N. S. C. MILLAR, A.R.I.C.*
and
C. H. BUCK, B.Sc. (Hons.),*

A Paper presented to the 2nd International Enamelling Congress, Leamington Spa, 1955

Introduction

THE behaviour of enamels in production depends on a variety of factors, which are summed up in the term "workability." Viscosity and surface tension are two important properties involved in this general term "workability" and in order to explore the mechanism of the enamelling process it is essential to study these factors separately.

In this paper an apparatus is described which is being used for measuring the viscosities of enamels and some of the results which have been obtained. An attempt has also been made to correlate viscosity measurements with flow, fusion point and firing range.

Viscosity Measurement

There are three fundamental methods of measuring absolute viscosity, namely:—

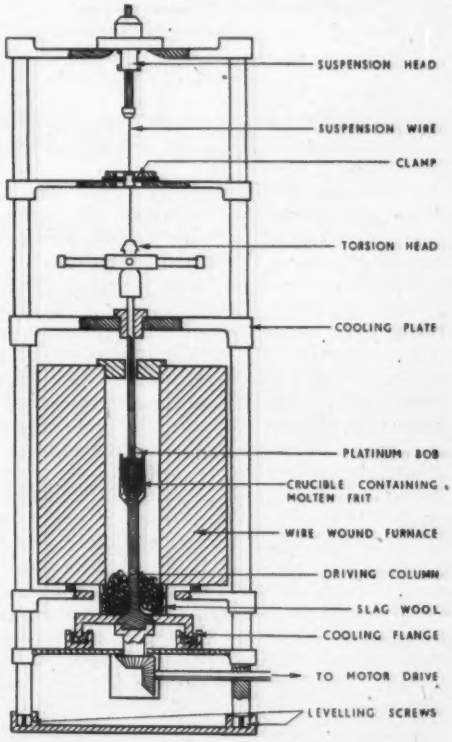
1. By measuring the flow through a capillary tube.
2. By measuring the torque on one of two concentric cylinders when one cylinder rotates in or around the fluid.
3. By measuring the rate of fall of a sphere through the fluid.

In each method it is necessary that the dimensions of the apparatus should remain constant and of known values during a measurement and the fluid under examination must not change in composition during a series of measurements. These requirements are not easily met at those temperatures at which enamels and glasses become fluid. Moreover, at such temperatures it is difficult to measure fluid flow rates and falling spheres can only be observed indirectly. Consequently most of the work on viscosities of glasses has been done by one form or another of the concentric cylinder methods. Typical examples of such researches may be found in the literature (1, 2, etc.).

The apparatus used by the authors is based largely on the apparatus designed by Lillie(3) for the measurement of viscosities of glasses at temperatures up to 1500°C. The apparatus is shown diagrammatically in Fig. 1 and is designed to enable the torque on the stationary inner cylinder to be measured when the outer cylinder is driven at a constant angular velocity.

The apparatus is carried on a framework comprising three vertical steel pillars. Triangular plates threaded on the pillars can be locked at any height and serve to carry the various com-

Fig. 1.—Diagram of viscosity apparatus.



*Radiation Ltd.

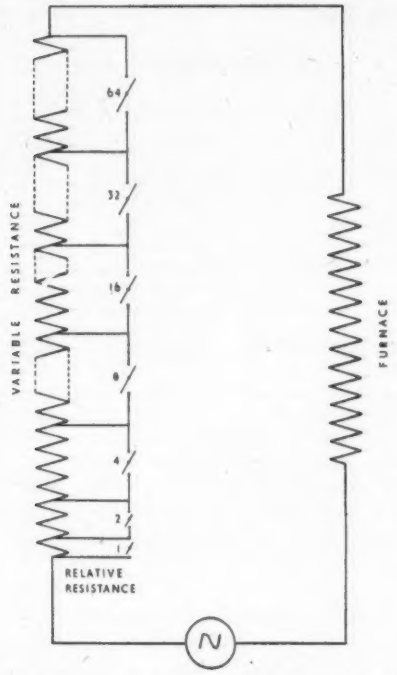


Fig. 2.—Diagram of simple variable resistance of robust design.

ponents. Levelling screws are provided at the base to enable the cylinders to be adjusted to concentricity.

At the base of the apparatus is a gearbox containing a worm and worm wheel. The worm is connected through another gearbox which includes reversing gear to a synchronous electric motor. The worm wheel is mounted on a vertical spindle the upper part of which is made of the heat-resisting alloy Nimonic 75. Between the upper and lower parts of the spindle is a water-cooled flange which protects the gearbox. The upper extremity of the Nimonic spindle is formed into a tapered cup. Surrounding the Nimonic column is the furnace, wire wound on a Sillimanite tube and insulated with alumina powder. The power input to the furnace may be controlled by a thermostatic system, but up to the present it has been found sufficient to use a Sunvic energy regulator, by means of which the furnace can be made to maintain any given temperature for short periods, or alternatively to rise or fall steadily in temperature. The gap between the furnace and the Nimonic column is sealed at the base with glass wool to prevent air flow and excessive heat loss through the furnace.

The variable resistance (Fig. 2) described below was constructed for manually controlling the temperature of the electric furnace and is suitable for applications where thermostatic control is not appropriate.

The resistance consists of nickel-alloy wire wound on a hollow refractory former which is mounted vertically to encourage cooling by natural convection. The winding is tapped at unequal intervals each section being half the resistance of the following section. The tappings are taken to standard tumbler switches which can be used to short-circuit the individual sections. In this way it is possible to construct an adjustable resistance having 7 switches by means of which the value of the resistance can be set to any one of 128 different values. The use of tumbler switches gives precise setting of the resistance in a much more convenient and reliable way than the conventional sliding contact.

The Nimonic cup is situated halfway up the furnace in a region where the temperature is uniform over a height of several inches. Sillimanite crucibles are ground on the outside to fit the Nimonic cup and these are used to contain the molten enamel, and to form the outer cylinder of the viscometer.

The inner cylinder of the viscometer is a hollow cylinder of platinum, attached to a Nimonic tube. A thermocouple is mounted inside the platinum cylinder; the leads are carried in twin-bore silica tube and the remaining space is filled with alumina powder. Potentiometer leads are clipped on to the thermocouple ends when it is desired to measure the temperature of the inner cylinder and hence of the enamel in contact with it.

The platinum cylinder and its Nimonic stem are suspended from the top of the framework by an elastic suspension, consisting of two phosphor-bronze wires. The upper wire is finer than the lower wire, and the junction of the wires may be clamped. In this way the torsional stiffness of the suspension can be readily changed during a test. This enables a wide range of viscosities to be measured with one setting of the apparatus.

At the junction of the Nimonic stem and the lower torsion wire is fitted a small concave mirror to enable the deflections of the torsion suspension to be accurately measured by means of a conventional lamp and scale. Provision is also made at this point for attaching weights by which means the moment of inertia of the suspended system may be varied by known amounts, and hence the elasticity of the torsion wire may be determined by measuring the period of torsional oscillation of the suspended system.

Let I_0 be the unknown moment of inertia of the system;
t_0 be the period of torsional oscillation;

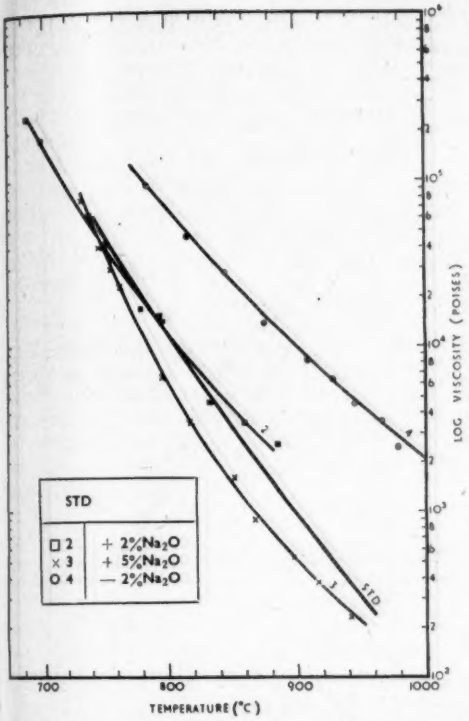


Fig. 3.—Viscosity curves of three frits containing additions of Na_2O compared with a standard.

I_1 be the change in moment of inertia produced by an alteration in the system of added weights;
t_1 be the new period of oscillation;
K be the elastic constant of the suspension.

Then $$t_0 = 2\pi \sqrt{\frac{I_0}{K}}$$

and therefore

$$K = \frac{4\pi^2 I_1}{t_1^2 - t_0^2}$$

Having determined the elastic constant of the suspension the apparatus is set up for a viscosity determination by introducing the Sillimanite crucible containing the molten enamel. To save time this is usually preheated in a separate furnace. The viscometer furnace is raised to the highest temperature required, usually about 900°C. and the controller is set so that the enamel temperature falls steadily at about 30°C. per hour. The crucible is rotated by means of the motor and gear drive and the deflection of the suspended system is measured by means of the lamp and scale. The reverse gear enables the deflections to be observed in both directions, thereby eliminating errors caused by asymmetry of the apparatus.

Let T be the torque on the inner cylinder,
and θ be the angular deflection of the suspended system.
Then $T = K\theta$
Let μ be the coefficient of viscosity of the fluid;
ω be the angular velocity of the outer cylinder;
a be the radius of the inner cylinder;
b be the radius of the outer cylinder;
l be the immersed length of the inner cylinder.

Then $$T = \frac{4\pi\mu\ a^2b^2}{b^2 - a^2} l\omega$$

The quantity

$$C = \frac{4\pi\ a^2b^2}{b^2 - a^2}$$ is defined as the constant of the apparatus and is calculated from the dimension of the two cylinders.

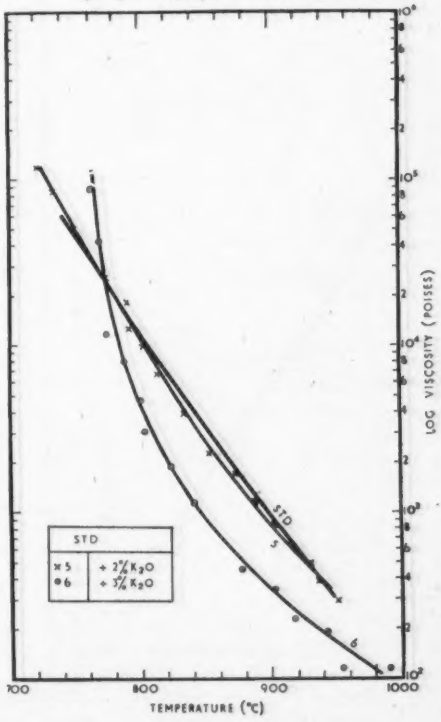
Then $$T = C\mu\, l\omega = K\theta$$

$$\therefore \mu = \frac{K\theta}{Cl\omega}$$

Preliminary Viscosity Measurements

Using the rotational viscometer the viscosities

Fig. 4.—Viscosity curves of two frits containing additions of K_2O compared with a standard.



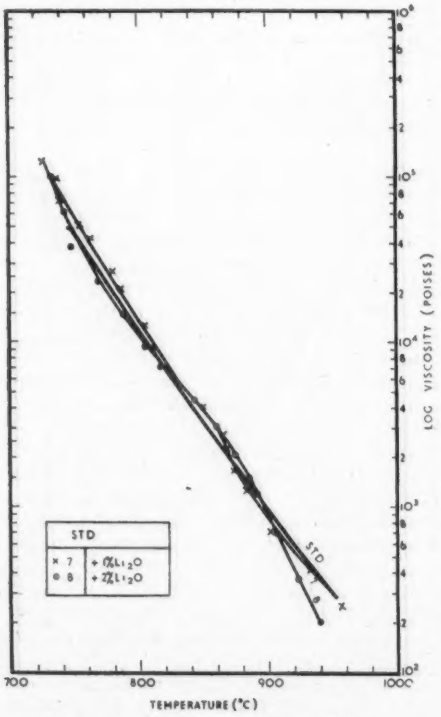
of a series of standard enamels which have been, or are in regular production on cast and sheet iron, were measured over the temperature range 750°C. to 900°C.

General conclusions drawn were:—

1. The viscosities of AR sheet-iron groundcoats were up to ten times the value of soft sheet iron groundcoats at 750°C. but at 850°C. this ratio had decreased to approximately 2½ to 1, all being less than 2,500 poises at this latter temperature.
2. The non AR sheet iron groundcoats had the lowest viscosity of all types of enamels examined.
3. The highest viscosities were found in the cast-iron AR blacks and the old type AR titania self-opacified sheet-iron enamels.
4. The AR cast-iron antimony-opacified enamels were not necessarily more viscous than the non AR antimony frits.

This preliminary investigation revealed the wide range of viscosities covered by the various types of enamel finishes and as a consequence it was decided to concentrate on one class of frit, namely, AR titania self-opacified enamels. This was further restricted to one particular formulation which is known to have quite good "all-round" properties. The scope of the investigation was widened by correlating viscosity with firing range, flow and fusion point. The ingredients of the base frit were varied to determine the influence of composition on these properties.

Fig. 5.—Viscosity curves of two frits containing additions of Li_2O compared with a standard.



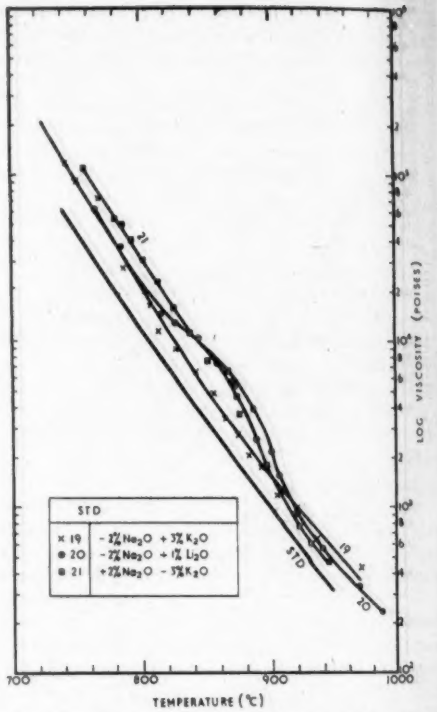


Fig. 6.—Viscosity curves of three frits containing additions of Na_2O and K_2O and Na_2O and Li_2O., compared with a standard.

Firing Range

This was determined by milling the frit with a standard mill addition, spraying on to six ground-coated sheet-iron panels to a constant weight and firing, for a fixed time, at temperatures of 750, 775, 800, 825, 850 and 880°C. in a laboratory muffle.

The colour, gloss and general appearance were then assessed to reveal differences in firing range.

Flow

Flow was measured by the fusion button method, based on that recommended by Marbaker(4). This consists of milling the frit to within predetermined limits, moistening with a 1 per cent solution of gum tragacanth, then pelletting to a cylinder 0.5in. × 0.5in. The pellets, placed on a

groundcoated panel, were fused in a muffle at 830°C. for 3 minutes, in a horizontal position, followed by 7 minutes at an angle of 60 deg. The product of maximum length and maximum width of the fused button was taken as a measure of enamel flow.

The standard frit was included in each firing and in the table of results the standard has been rated as 10, all other frit flow areas being amended by a factor to make all firings comparable and hence eliminate possible firing temperature variations.

Fusion Point

This comparative property was determined by placing a spherical pellet of frit, ground to between 150 and 200 mesh, on to a Nichrome wire ring and heating at a constant rate of 3°C. per minute. The temperature at which the frit had flowed through the ring was regarded as its fusion point.

Frit Modifications

The standard frit had the following melted composition:—

Na_2O	8.0
K_2O	4.0
Li_2O	0.5
Al_2O_3	1.5
B_2O_3	12.0
Si_2O	48.0
TiO_2	20.0
Na_2SiF_6	6.0
	100.0

Modifications to the per cent melted composition consisted of:—

+2 per cent Na_2O; + 5 per cent Na_2O, —2 per cent Na_2O
+2 per cent K_2O; + 3 per cent K_2O
+1 per cent Li_2O; + 2 per cent Li_2O; —0.5 per cent Li_2O

TABLE I

EFFECT OF FRIT COMPOSITION ON FLOW, FUSION POINT AND FIRED ENAMEL

Frit	Variation	Flow	Fusion Point °C.	FIRED ENAMEL		
				COLOUR	GLOSS	GENERAL APPEARANCE
1	NIL	10	740	Standard White	Good	Good
2	+ 2% Na_2O	7.6	790	Cream	Inferior at high temps.	Decrease in opacity
3	+ 5% Na_2O	5.3	810	Cream	Inferior at high temps.	Decrease in opacity Brown patches on panels fired above 800°C.
4	— 2% Na_2O	6.6	815	Sl Pink	Brilliant	superior colour stability.
5	+ 2% K_2O	7.7	790	equals standard	equals standard	equals standard
6	+ 3% K_2O	7.8	785	Sl Cream	Sl inferior	equals standard
7	+ 1% Li_2O	10.3	734	Cream	equals std	equals standard
8	+ 2% Li_2O	9.4	770	Deep Cream	inferior	equals standard
9	—0.5% Li_2O	9.0	760	Sl Pink	equals std	equals standard
10	+ 2% B_2O_3	11.3	734	equals std	superior to std at low temps.	" "
11	+ 5% B_2O_3	12.2	729	Cream	Inferior	poor colour stability.
12	— 5% B_2O_3	7.2	785	Sl Pink	Sl superior	Equals Standard
13	+ 2% SiO_2	10.3	772	Sl Grey	Sl superior	" "
14	+ 5% SiO_2	10.0	745	Sl Grey	Sl superior	" "
15	— 3% SiO_2	9.0	740	equals std	Superior between 825 & 880°C. fire	Superior colour stability.
16	+ 2% TiO_2	10.7	757	equals std	superior	equals standard
17	+ 2% F_2	11.8	726	Sl Pink	superior	" "
18	+ 2% Al_2O_3	8.0	815	equals std	equals std	" "
19	—2% Na_2O+ 3% K_2O	11	740	" "	" "	" "
20	—2% Na_2O+ 1% Li_2O	9.2	765	Sl Cream	" "	" "
21	+2% Na_2O— 3% K_2O	10.4	770	Equals Std	" "	" "
22	—3% SiO_2 + 4% TiO_2	10.0	770	" "	Sl superior at lower temps.	" "

NB.—The initial slumping of the frits containing increased alkali exceeded that of the standard frit.

TABLE II

FIRING RANGE

FRIT	VARIATION	FIRED 6 MINS. AT					
		750°C.	775°C.	800°C.	825°C.	850°C.	880°C.
1	NIL	S1 UF	OK	OK	S1 OF	OF	OF
2	+ 2% Na_2O	OK	OK	S1 OF	OF	OF	OF
3	+ 5% Na_2O	OK	S1 OF	OF	OF	OF	OF
4	— 2% Na_2O	S1 UF	OK	OK	OK	S1 OF	OF
5	+ 2% K_2O	OK	OK	OK	OF	OF	OF
6	+ 3% K_2O	OK	OK	OK	OF	OF	OF
7	+ 1% Li_2O	OK	OK	S1 OF	OF	OF	OF
8	+ 2% Li_2O	S1 OF	OF	OF	OF	OF	OF
9	— 0.5% Li_2O	S1 UF	OK	OK	OK	OF	OF
10	+ 2% B_2O_3	OK	OK	OK	S1 OF	OF	OF
11	+ 5% B_2O_3	OK	OK	S1 OF	OF	OF	OF
12	— 5% B_2O_3	UF	OK	OK	OF	OF	OF
13	+ 2% SiO_2	S1 UF	OK	OK	SI OF	OF	OF
14	+ 5% SiO_2	S1 UF	OK	OK	OK	OF	OF
15	— 3% SiO_2	OK	OK	OK	S1 OF	OF	OF
16	+ 2% TiO_2	S1 UF	OK	OK	OK	OF	OF
17	+ 2% F_2	OK	OK	OK	S1 OF	OF	OF
18	+ 2% Al_2O_3	UF	OK	OK	S1 OF	OF	OF
19	— 2% Na_2O + 3% K_2O	S1 UF	OK	OK	S1 OF	OF	OF
20	—2% Na_2O + 1% Li_2O	OK	OK	OK	S1 OF	OF	OF
21	+ 2% Na_2O — 3% K_2O	OK	OK	OK	S1 OF	OF	OF
22	— 3% SiO_2 + 4% TiO_2	OK	OK	OK	OK	OF	OF

UF + Underfired.
OK — Correctly fired.
OF — Overfired.

+2 per cent B_2O_3; + 5 per cent B_2O_3; —5 per cent B_2O_3
+2 per cent SiO_2; + 5 per cent Si_2O; —3 per cent SiO_2
+2 per cent TiO_2
+2 per cent Al_2O_3
+2 per cent F_2
—2 per cent Na_2O+3 per cent K_2O } *i.e.* equi-
—2 per cent Na_2O+1 per cent Li_2O } molecular
+2 per cent Na_2O—3 per cent K_2O } replace-
—3 per cent SiO_2+4 per cent TiO_2 } ments.

Results

The viscosity curves for 11 of these frits are shown in Figs. 3 to 6. The flow, fusion point and firing range are given in Tables I and II.

Conclusions

1. Viscosity is decreased with increase in alkali content, but the relationship is not linear and its form depends on the particular molecules concerned.
2. Increase in Na_2O causes greater viscosity variation with temperature while decrease in Na_2O causes less viscosity change with temperature.
3. Increasing the Li_2O causes a more constant viscosity between 800 and 880°C. but outside these limits the viscosity variation with temperature increases.
4. Increasing the K_2O causes a more fluid enamel between 770 and 1000°C. but at lower temperatures the viscosity is greater than that of the standard frit. The effect of 3 per cent K_2O is greater than that which occurs with a 5 per cent Na_2O increase.
5. The increase in alkalis causes an increase in fusion point; the 1 per cent lithia increment being an exception and causing a slightly softer enamel.
6. B_2O_3 and fluorine increments cause a decrease in fusion point.
7. Decreasing the Na_2O and increasing the Al_2O_3 have the greatest hardening effect.
8. Increasing the Na_2O and K_2O cause the flow to decrease although the initial slumping of the horizontally fired pellet is greater.
9. The 1 per cent lithia increment causes slightly superior flow whereas larger lithia additions cause a slight decrease in flow.
10. Flow is considerably increased by additions of B_2O_3 to the frit.
11. Varying the silica and titania content within the stated limits has little effect on flow.
12. Increasing the fluorine content causes increased flow.
13. Molecular replacements of the alkali metals have a small effect on flow but this bears no relationship to the fusion point changes.

(*Continued in page 160*)

NUMBER SIX

METAL FINISHING RESEARCH
A Survey of its Organization, Existing Facilities and Current Work

The Work of The Corrosion Section at Fulmer Research Institute

WITH corrosion taking such a devastating annual toll of the resources of the nation, increasing attention is naturally being paid in laboratories throughout the United Kingdom to analysing the causes of attack of particular materials and where possible prescribing remedial measures. Coupled with the 'natural' wastage in rural, home, industrial or marine environments, the problems to be faced in situations where the combined effects of applied stress, either static or cyclic in fatigue, and corrosion occur, are daily on the increase. These latter problems of stress corrosion and corrosion fatigue (in which failure occurs much more rapidly than could be expected from the summed effects of the separate agents) are the more disturbing since there is frequently a total absence of outward visible symptoms of decay. Patient investigation in the laboratory supported by extensive trials at suitable field-test sites is slowly providing the answers to many corrosion problems in the form of new protective finishes, cathodic protection, etc.

The importance of field tests cannot be underestimated, since the complex reactions obtaining in, for example, the corrosion of aluminium alloys must be treated and examined with caution. Although accelerated laboratory tests are widely used, at Fulmer as elsewhere, care is necessary in the interpretation of results. Slight changes in incompletely understood variables may occasion effects not experienced in practice; reaction products may differ and application of the results of these accelerated laboratory tests to assess the suitability of particular materials for long-term service under specific conditions requires care. The presence or absence of impurities in the corroding agents used may result in depolarizing or inhibiting action, with consequent modification of the corrosion rate; edge effects, surface preparation and experimental arrangement with regard to such things as atmosphere renewal, disposition of condensates on the test specimens, etc. are also important and require careful control. Nevertheless, accelerated tests are of considerable value when coupled with wide experience.

Fig. 1. — Apparatus for carrying out accelerated stress corrosion tests under laboratory conditions.

It will be appreciated that much of the work at Fulmer cannot be described in detail since all investigations are undertaken on a "confidential to the sponsor" basis. In some cases, however, sanction is given by the private sponsor for publication of the results and in others it is generally permissible to indicate the nature of the problems being tackled. The following brief account of the corrosion section at Fulmer during the past three years will serve to indicate some of the ways in which the Institute is endeavouring to serve British industry. In providing facilities for confidential research, development work and the investigation of *ad hoc* problems, it enables individual firms to secure for themselves the com-

Fig. 2.—Simple rigs for carrying out stress corrosion tests in the field.

mercial benefits which may accrue from what is a strictly private examination and report on their problems.

Fulmer as an integrated metallurgical research laboratory possesses much equipment which proves invaluable in supplementing the direct resources of the corrosion section in their experimental investigations. The facilities of the analytical laboratories, together with the spectrograph, require no explanation of their use in identifying corrosion products, etc. The metallurgical microscopes are one means of examining the nature and extent of corrosive attack and are also used to measure the quality, thickness and uniformity of electroplated and other deposits such as anodic films, hot-dip coatings, etc. Internal stress in protective deposits or basis materials can be asserted with the aid of the X-ray diffraction units and the forthcoming installation of an electron microscope will add to the useful experimental techniques available. For its mechanical-testing and fatigue-testing requirements the corrosion group works in close collaboration with the mechanical engineering group, which also assists in the design and construction of stress-corrosion rigs or other specialized apparatus.

Under the direct control of the corrosion section itself are the various units for salt-spray testing, the accelerated SO_2 exposure test, humidity cabinets, etc., and chambers for special environment tests. In addition it has experimental scale electroplating facilities, and the necessary apparatus for measuring coating thickness (by the B.N.F. jet test for example) abrasion resistance, etc.

There are stress-corrosion rigs for laboratory tests in direct tension or bending and similar simple rigs for exposure of stressed specimens at the field sites in Sheffield (heavy industrial atmosphere), Hayling Island (marine), Fulmer (rural) and Christchurch (tidal river stretches). Normal unstressed exposure tests are also conducted at these sites.

Among the major research projects conducted by the corrosion section, an examination of the corrosion and stress-corrosion behaviour of aluminium alloys [1, 2] has always been prominent, but in view of the published information about these investigations it is not proposed to describe them further here.

Related work concerns protective finishes on aluminium alloys and investigations dealing with electroplated coatings, quality and effectiveness of anodized finishes, and the evaluation of paint schemes for corrosion protection in particular environments.

Preparation of hard surfaces on steel by such processes as siliconizing has also been the subject of an extensive investigation, now completed, and other major problems concern the blackening of aluminium and its alloys under fretting conditions, and an examination of chromium plating baths. The last named is associated with Fulmer's programme on high-temperature materials in which a study of the preparation and properties of ductile chromium forms an important part.

Ad hoc investigations involving corrosion troubles are constantly being received. Some of these are relatively straightforward and attention to the technical literature already available on particular problems might have prevented many from occurring, or at least provided the remedy without recourse to the Institute. Defects arising from improper cleaning prior to plating

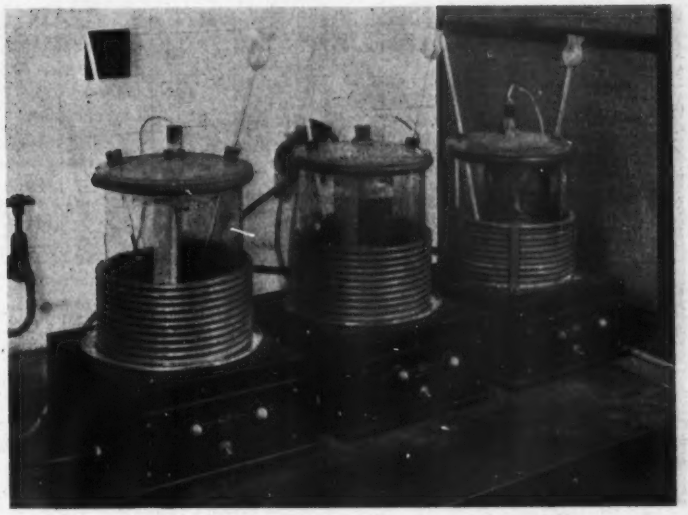


Fig. 3. — Special atmosphere exposure chambers.

or from inadequate coatings or coating technique are fairly common and such troubles as the staining of cadmium plated parts due to non-removal of plating solutions and/or non-passivation, or electro-chemical attack in bi- or multi-metal systems, also arise from time to time. Other more interesting and extensive investigations still of an *ad hoc* nature have been concerned with such problems as the corrosion of "dry" compressor pumps due to condensation during shut-down periods; an evaluation of water contamination by domestic boiler materials; an examination of such processes as shellac finishing and "electroless" nickel plating for specific components; and the comparative examination of paint finishes for chemical plant.

Attention, in the form of reviews of the literature, has also been paid to such diverse topics as the colour fastness of dyed anodized aluminium; materials for application in orthopaedic surgery (*i.e.* for internal fixation of fractures where corrosion by body fluids and general 'sympathy' with healing processes must be considered) and finally to probes for evaluating corrosion of stack materials by flue gases.

In concluding this brief account of the activities of the corrosion section at Fulmer Research Institute the other services available to industry should not be forgotten. Primarily concerned with metallurgical engineering, the Institute has established physical metallurgy, physical chemistry (dealing largely with extraction problems) foundry, physics, engineering and mechanical testing, and analytical sections in addition to the corrosion group. The problems which it is prepared to tackle are not, however, confined to the metallurgical engineering field. Investigation of many problems completely divorced from the major field has, in fact, been successfully undertaken: Measurement of insulating properties of foamed plastics and other non-metallic materials, and assessment of filter characteristics are currently under way, for example. It remains only to restate that each enquiry which the Institute receives, whether it results in investigational work or not is treated on a confidential basis. The results of the investigations undertaken, including any patents arising from them, belong entirely to the sponsor who pays for the cost of work carried out on his behalf.

References

(1). Metcalfe, G. J. *Jnl. Inst. of Metals*, 1952-53, **81**, p. 269.
(2). Liddiard, E. A. G. and Bell, W.A. *Jnl. Inst. of Metals*, 1953-54, **82**, p. 236.

ELECTRODEPOSITED IRON-ZINC ALLOYS

The annual report of the British Iron and Steel Research Association recently published, makes some references to the investigations into surface coating techniques being carried out by the Association's laboratories at Sketty Hall, Swansea. An agreement has now been made with Silvercrown Ltd., for the commercial development of electrodeposited iron-zinc alloys, a process which was developed at the Swansea laboratories.

Some accounts of the properties of these alloys have appeared in the literature from time to time, and indicate that they are attractive in appearance, hard wearing, and not easily damaged by deformation. They lend themselves to plating at high speeds and have a useful smoothing action. Alloys with from 35 to 65 per cent zinc appear from corrosion tests to have as great a resistance to atmospheric corrosion as does pure zinc.

These results show that viscosity alone does not determine flow or fusion point and hence the workability of the enamel.

Practical Application

These results have been utilized to improve the workability of a superopaque titania enamel applied to cast iron. The original frit during smelting was extremely fluid and it was difficult to obtain a thread in the usual test for "batch freeness"—the melt falling off the dip rod in drops.

This frit exhibited excessive boiling when fired. By increasing the silica content of the frit the melt flowed from the dip rod as a thread and on firing there was complete absence from boil.

Theory

It is known that in this type of enamel the network formers consist of silica, boron oxide and titania while the alkalis act as network modifiers. The action of the network modifier is to increase the distance between the silicon, boron or titanium and the surrounding oxygen ions, this usually causing a viscosity decrease(5). An atomistic interpretation of the effect of composition on the viscosity of glass is given by Marbol and Weyl(6).

Partial replacement of oxygen by fluorine results in a decrease in viscosity of the enamel. This fact may be explained by the increase in ratio of anion to cation, two F^- replacing one O^{--}(6).

When titania is smelted into a normal alkali metal borosilicate type enamel, the fluidity of the smelt often increases and provided no TiO_2 crystallizes on firing, the fluidity on firing also increases. This may be due to the formation of sodium titano silicate, a very fluid liquid at about 1100°C.

In any one enamel it would appear from the investigations described in this paper that there is a critical amount of glasswork modifier which can be incorporated to cause a decrease in fluidity. Beyond this critical limit the mobility of the glass decreases. The standard enamel chosen would appear to be very close to the critical modifier/former ration in that all the alkali additions, except the lowest lithia increment, caused a decrease in enamel flow. These alkali additions did not, however, cause any noticeable decrease in fluidity of the smelt before quenching. At the smelting temperature the titania is in solution and acts as a network former. The network modifier/former ratio is then below the critical limit. On firing, a large proportion of the titania crystallises out and no longer acts as a network former and hence the critical limit of modifier/former in the remaining glass has been exceeded. The rapid initial slump of the frits containing increased alkalis can be explained by the fact that the titania had not yet recrystallized. Increasing the B_2O_3 or slightly increasing the silica restores the modifier/former ratio to below the critical limit after crystallisation of the titania and thus causes an increase in fluidity.

In similar enamels free from titania and in those which were saturated but not supersaturated with titania an increase of 5 per cent soda did not cause a decrease in flow.

In the standard frit the incorporation of calcia and baria again caused a decrease in flow, the two oxides acting as network modifiers in a similar manner to the oxides of sodium potassium and lithium.

It is realized that the work described in this paper is limited to one composition in one class of vitreous enamel. The theory postulated to explain the unusual effects noted, is only a working hypothesis and may require amending as this investigation continues. The influence of surface tension has not been examined and it is felt that this is of major importance in the complete understanding of enamel behaviour on firing. Also no attempt has been made in this paper to explain viscosity and flow in terms of ionic radii and charge of the glass constituents, owing to insufficient data at the present time but it is hoped that this will be rectified in future work.

In conclusion the authors wish to express their thanks to Mr. P. E. Pearson and Miss Blencowe for assistance in the practical work and also to the Directors of Radiation Ltd., for permission to publish this paper.

References

(1) Washburn, Libman and Shelton. "The viscosities and surface Tensions of the Soda-Lime-Silica Glasses at high temperature." University of Illinois, Eng., Expt., Sta., Bulletin No. 140 (1924).
(2) English S. "The effect of Composition on the Viscosity of Glass" (Part II). *Society Glass Technology* 1924, 8 (31) p.205.
(3) Lillie, H. R. "The Measurement of Absolute Viscosity by the use of Concentric Cylinders". *American Ceramic Society*, 1929 August (505).
(4) Marbaker, E. E. "Improvements in the Button Test for Determination of Frit Fluidity". *J. American Ceramic Society*. 1947. 30 (12) 354.
(5) Laithwaite, H. "Some properties of Vitreous Enamels and their Practical Significance". *Proc. of Inst. of Vit. Enam.* 11 p.115.
(6) Marbal, E. C. and Weyl, W. A. "An Atomistic Interpretation of the Effect of the Composition of the Viscosity of Glass". *J. Soc., Glass Tech.*, 34, (186) p.16T.

Anglo S.A. Pigment Plant Project

It has been announced by British Titan Products Co. Ltd., of York, and African Explosives and Chemical Industries Ltd. of Johannesburg, S.A., that they have formed a new joint company in South Africa. The erection at Umbogintwini, on the Natal South Coast some 17 miles from Durban, of a plant to manufacture titanium-dioxide pigments is now well advanced. It is intended that the plant will reach the production stage towards the end of 1958, and it has been designed to meet the whole of the growing demand in Southern Africa for titanium dioxide, a product which was previously imported.

FINISHING NEWS REVIEW

FORTHCOMING INTERNATIONAL MEETINGS

FOURTH INTERNATIONAL GALVANIZING CONFERENCE

As announced last month the Fourth International Conference on Hot-Dip Galvanizing will be held in Milan from June 11-13. In this country responsibility for the organization of the Conference rests with the Zinc Development Association, 34, Berkeley Square, London, W.1., to whom all correspondence in connexion with the Conference should be addressed. Reservations for travel and hotel accommodation are in the hands of Thomas Cook and Son Ltd.

Prior to the opening of the Conference on Monday, June 11, there will be an informal reception for delegates and ladies on Sunday evening in the Sala delle Colonne in the Museo Nazionale della Scienza e della Tecnica. This building will be the headquarters of the Conference.

The programme of the technical sessions is as follows:—

Monday, June 11.

9.30 a.m. Official opening of Conference.

10.00 a.m. *First Technical Session.*

1. "Review of Galvanizing Bath Performance in 1955." By D. N. Fagg.
2. "Productivity Improvements in U.K. Galvanizing Works." By A. G. Northcott.

11.30 a.m. *2nd Technical Session.*

3. "The Painting of Hot Dip Galvanized Steel." By V. J. E. van Eijnsbergen.

12.30 a.m. Meeting adjourns.

Tuesday, June 12.

9.30 a.m. *3rd Technical Session.*

4. "Heat Consumption and Performance of Modern Galvanizing Baths." By Dr. Wubbenhorst.
5. "Electrical Resistance Heating." By R. Gloor.
6. "Lead-jacketed Gas Heating." By L. F. Chambers.
7. "Low-frequency Induction Heating."

11.00 a.m. *4th Technical Session.*

8. "Galvanizing Pot Construction."
9. "Effect of Impurities in Iron on Attack by Molten Zinc." By D. Horstmann.

12.30 a.m. Meeting adjourns.

Wednesday, June 13.

9.30 a.m. *5th Technical Session.*

10. "The Galvanizing of Wire Netting." By C. Lepage.
11. "The Galvanizing of Cast Iron." By S. A. Hiscock.
12. "Galvanizing of Angle Sections."

11.30 a.m. *6th Technical Session.*

12. "New Markets for Galvanizing." By R. L. Stubbs.

Social Functions and Excursions

On June 11, starting at 2.30 p.m. there will be a coach tour to Lake Como. There will be a short stop at Como for a visit to the Cathedral and the Volta Museum, and dinner will be taken at the famous Grand Hotel Villa d'Este overlooking the Lake at Cernobbio. The following day there is an excursion for ladies in the morning by coach to Dertosa di Pavia, a famous Carthusian monastery containing many paintings and other interesting works of art.

The formal proceedings of the Conference are concluded on June 13 by a Conference Banquet for delegates and ladies, at the Odeon Restaurant.

Works Visits

Several of the leading galvanizing firms in Italy, and one in Switzerland, have extended invitations to Conference delegates to visit their works, most of which have either been built or largely modernized during the last few years.

Among the firms who have extended invitations are: S.p.A. Cornigliano, Oscar Sinigaglia Works (near Genoa) (Sendzimir sheet galvanising), S.p.A. Dalmine, Dalmine Works (near Milan), Torre Annunziata Works (near Naples) (tube galvanizing), S.p.A. Giuseppe and Fratello Redaelli, Acciaierie e Ferriere, Rogoredo Works (near Milan) (wire galvanizing), S.p.A. Acciaierie Ferriere Lombarde Falck (near Milan) (wire galvanizing), Verzinkerei Zug (Switzerland) (general galvanizing), S.A. Montevecchio, Porto Marghera Works (near Venice) (zinc production), Soc. Vittorio Necchi, Pavia Works (near Milan), (production of iron castings and sewing machines).

"SURFACE TREATMENT FOR THE IMPROVEMENT OF MECHANICAL PROPERTIES AND PROTECTION AGAINST CORROSION"

6th International Mechanical Engineering Congress

Commencing on June 4 a comprehensive series of papers will be discussed at the Sixth International Mechanical Engineering Congress at 11, Avenue Hoche, Paris.

Detailed information, programme, and registration forms for this Conference may be obtained in the U.K. from the British Engineers Association, 32, Victoria Street, London, S.W.1.

The titles of the various sections under which the Working Sessions are organized and their various chairmen are as follows:—

Section A.1. Improvement of resistance to wear by increase of surface hardness. Dr. H. E. Z. Gordon (U.K.).

Section A.2. Improvement of resistance to wear through improvement of friction characteristics. Mr. H. Chalvet (France).

Section B. Improvement of resistance to heat. Prof. E. Rudberg (Sweden).

Section C.1. Improvement of resistance to corrosion by metal coatings deposited by means other than electroplating. Dr. Ing. Giuseppe Prever (Italy).

Section C.2. Improvement of resistance to corrosion by electroplating processes. Mr. C. Van Rooy (Belgium).

Section C.3. Improvement of resistance to corrosion by chemical processes. Mr. Roger Studler (France).

Section C.4. Improvement of resistance to corrosion by non-metallic coatings. Dr. A. L. Saboz (Switzerland).

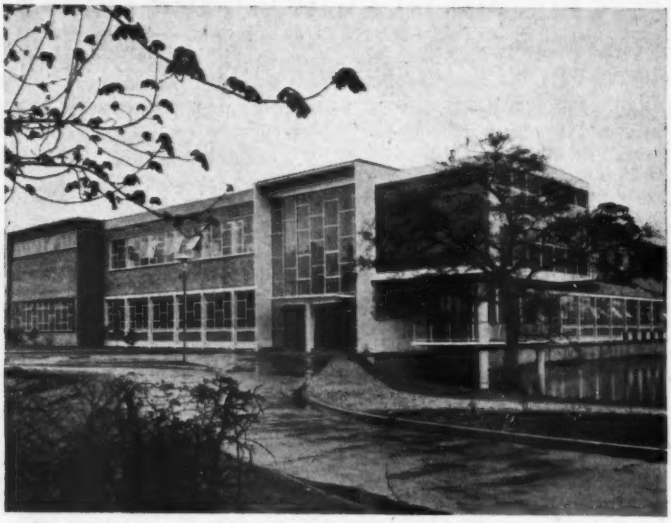
Section D. Surface treatment for decoration and for improving optical properties. Dr. S. Wernick (U.K.).

Other arrangements include a number of factory visits and several social receptions and the culminating Congress dinner on June 8 at Chantilly.

RESEARCH INTO RESIN

New Technical Service Laboratories

ON May 3 a new £300,000 technical service laboratory for the Shell Chemical Co Ltd., was opened at Egham, by the Rt. Hon. Sir Lionel Heald, P.C., Q.C., Member of Parliament for the Chertsey Division of Surrey. The opening ceremony was preceded by a luncheon at the laboratories at which Mr. F. A. C. Guepin, managing director of the Royal Dutch Petroleum Co. and chairman of Shell Chemical Co. Ltd., presided.



Above: A general view of the new technical service laboratory building of the Shell Chemical Co. Ltd., at Egham.

Below: The surface coatings laboratory devoted to the investigation of all problems connected with the formulation and application of paints, varnishes and lacquers.

The purpose of the laboratories is to provide technical service to the many customers of the company in the fields of surface-coating materials, detergents, resins and general chemicals derived from petroleum.

The laboratory itself stands in the grounds of Rusham House, an old Surrey country house, and is bordered on one side by a small lake. The organization provides for a separate laboratory devoted to each of the principal fields, together with workshops where problems can be investigated on a scale comparable with that obtaining in industry. Thus there is a resin laboratory, at present primarily concerned with investigating and solving problems arising from the use of "Epikote" resins in plastics applications, and a detergents and general chemical laboratory, with which are associated a market development workshop whose functions are to prepare sample lots and investigate the processing of thermosetting resins.

Surface-Coatings Laboratory

The surface-coatings laboratory is responsible for the investigation of all problems relating to paints, varnishes and lacquers and is equipped with the necessary research apparatus for this purpose. Its associated surface-coating workshop is in effect a paint factory in miniature, reproducing on a small scale the plant set-up of a modern paint factory. The equipment here includes a sand-blast cabinet, several ball mills, a three-roll paste mill, a change-pan mixer, and an edge runner for dry pigment mixing. Accelerated-breakdown test equipment is also installed in this workshop, and further facilities for performance testing are available in a constant-temperature room.

The broad functions of the surface-coatings laboratory are to carry out customer service work, and longer term work on the industrial application of solvents and resins, involving the formulation of paints, varnishes and lacquers and the examination of their physical properties. The actual manufacture of experimental coating materials is carried out in the surface-coatings workshop and these are then applied in separate spray and stoving rooms. The spray room is equipped

AND SOLVENT USAGE

for Shell Chemical Co. Ltd.

with a water-wash spray booth and is provided with filtered conditioned air. Three ovens are available in the adjacent stoving room for the curing of applied coatings.

Other general facilities include an analytical laboratory, a central library, and a large conference room.

Within the laboratory building, but independent of the technical service laboratories, is a laboratory devoted to fundamental and exploratory research, particularly in the field of organic reactions, under the direction of Sir Robert Robinson, O.M., F.R.S., winner of a Nobel Prize in 1947, well-known for his eminent contribution to organic chemistry, notably in the field of alkaloids, hormones and anti-biotics.

On his retirment last Autumn from the Wayneflete Professorship of Chemistry at Oxford, Sir Robert accepted a Directorship with Shell Chemical Company. Amongst his other activities he has at his disposal the upper wing of the Egham Laboratory. This research wing consists of Sir Robert's own private laboratory, a main research laboratory accommodating his team of research workers, and an optical instrument room housing two particularly noteworthy pieces of equipment. These are a Perkin-Elmer universal spectrophotometer, which operates over a wide wave-length from far ultra-violet to far infra-red, and a vapour-phase chromatograph capable of separating and identifying volatile compounds with very close boiling points.

Display Room

A particularly interesting and informative department of the laboratories is the display room designed to illustrate the chemical derivation, method of manufacture and industrial applications of all the chemicals (other than agricultural products) marketed by the Shell group of companies. The display comprises a series of illuminated panels showing the location of chemical plants, a large flow diagram illustrating the progressive manufacture of chemicals from refinery gases, together with a number of working models demonstrating some of the end uses of "Epikote" resins and other petroleum chemicals in surface coating and other industrial and domestic fields.

In view of the fact that the infant science of the derivation of complex-organic chemicals from petroleum by-products has already made significant if not revolutionary, contributions to the science of paint manufacture, it can confidently be expected that the work of these new laboratories, although not primarily devoted to fundamental research will be productive of still further notable advances in this field.

Above: The surface coatings workshop which is in effect a small-scale paint factory equipped to convert raw materials into all types of surface coatings.

Below: Part of the research laboratory directed by Sir Robert Robinson in which fundamental investigations into relevant organic reactions are carried out.

EDUCATION IN PAINT TECHNOLOGY

IN the recent White Paper on Technical Education, the Borough Polytechnic, Borough Road, London, S.E.1., was designated as one of the technical colleges recognized as centres of education in advanced technology. The Governors therefore invited the various bodies in the paint trade to nominate representatives to assist them in formulating an educational policy for the industry. The response was encouraging and an Advisory Committee representative of national opinion was formed consisting of the following nominated representatives: Mr. R. C. Good and Mr. C. Montague Smith, F.R.I.C. (London Colour, Paint and Varnish Manufacturers' Association); Mr. C. E. Rowe and Mr. R. Yeates (Society of British Paint Manufacturers); Mr. D. Roe and Mr. G. L. E. Smith (Paint Manufacturers' and Allied Trades' Association); and Dr. S. H. Bell, A.R.C.S., F.R.I.C., and Mr. H. A. Newnham, B.Sc. (Oil and Colour Chemists' Assn.).

In addition the following have been co-opted to the Committee: The Rt. Hon. Lord McCorquodale of Newton; Dr. R. F. Bowles, F.R.I.C.; Mr. G. Copping; and Mr. T. Drummond Kerr. The Governors have nominated from their number: Mr. T. G. Gibbings, M.B.E., J.P., and Mrs. O. U. Foss, B.A., who acts as Chairman.

The Staff members are Dr. D. H. Ingall, F.R.I.C., F.Inst.P. (the Principal), Dr. F. Aylward, F.R.I.C., head of the department of chemistry and food technology, Dr. P. M. Fisk, F.R.I.C., in charge of the paints section and Mr. F. J. Packer, A.C.I.S., A.M.I.I.A., the secretary to the Governors who acts as secretary to the Committee.

It is hoped that this strong committee, which represents interests in London and the provinces, will be able to assist on a national basis the development of courses at the Borough Polytechnic in advanced technology in the paint and similar industries.

SUMMER SCHOOL ON CORROSION

THE third Summer School on Corrosion, organized in conjunction with the Corrosion Group of the Society of Chemical Industry, will be held at Battersea Polytechnic this year from July 17 to 20. The topic will be "Water Treatment" and should be of interest to chemists, engineers and others who are concerned with this subject.

The lecture syllabus will deal with the following aspects of water treatment: "Types of Water and Their Properties," by C. W. Drane, B.Sc., F.R.I.C.; "Electrochemical Principles of Corrosion," by L. L. Shreir, Ph.D., F.R.I.C., F.I.M.; "Inhibition of Corrosion by Waters," by R. S. Thornhill, M.A., Ph.D., F.I.M.; "Materials of Construction," by W. D. Clark, M.A., M.Sc., A.I.M.; "Water Softening—Precipitation Methods," by A. H. Waddington, B.Sc., A.R.I.C., P.A.I.W.E.; "Water Treatment—Ion-Exchange Methods," by B. A. Sard; "Steam Boiler Feed Water Treatment," by P. Hamer, B.A., A.R.I.C.; "Circulating Water Treatment," by C. W. Drane, B.Sc., F.R.I.C.; and "Examples of Industrial Problems" by H. H. Burns, B.Sc., F.R.I.C. In addition to the lectures there will be demonstrations of methods of water treatment and control analysis while visits to a power station and water works have also been arranged. The inclusive fee for the Summer School is £4 4s. Accommodation is available at the Polytechnic Hostel for the period of the Summer School at an inclusive fee of £5 5s. Particulars can be obtained from the Secretary (Corrosion S.S.), Battersea Polytechnic, London, S.W.11.

REVO NAME CHANGE

The name of the Revo Enamel Co. which was changed earlier this year to the Tividale Enamel Co. has been changed again to the **Tipton Enamel Co.** The company remain at the same address: Groveland Road, Tividale, Tipton, Staffs.

EFCO LTD. OPEN NEW DEPOT IN BIRMINGHAM

Shown on the left is a view of the new depot recently opened by the Electric Furnace Co. Ltd., at Alexandra Avenue, Handsworth, Birmingham, 19. Arrangements have now been made for electroplating materials to be available for same-day delivery from stock in the Birmingham area by the Electro-Chemical Engineering Co. Ltd., while the Electric Furnace Co. Ltd., and Electric Resistance Furnace Co. Ltd., have also arranged for immediate after-sales service facilities, spares for Efco-Wyatt non-ferrous melting units being held in stock.

All enquiries should be made to the Birmingham Office of EFCO Ltd., at 43 Vittoria Street, Birmingham, 1.

B.B.C. AT ENAMEL WORKS

Vitreous Enamel as an Artistic Medium

DURING April there was staged at the Hanover Galleries an Exhibition of pictures painted by Stefan Knapp. Mr. Knapp's style is very much in the modern idiom and his use of colour is striking and effective. These qualities are, of course, shared by many present-day artists, but Mr. Knapp's unique claim to fame lies in his choice of vitreous enamels as his artistic medium.

Enamelling is an art whose origins are lost in the mists of pre-history and much of present-day enamelling technique has changed very little with the passing of centuries. In spite of this, however, and in spite also of the fact that enamels have found wide application in the decoration of metal surfaces, there have been very few recorded instances of their use as a medium in the painting of pictures, and certainly none on the scale achieved by Mr. Knapp.

Mr. Knapp's work is executed with brush and palette knife on both steel and copper sheets using orthodox industrial and jewellery-type enamels. Over the past year he has had the enthusiastic co-operation of the firm of Stewart and Gray Ltd., at whose works in Mitcham, the necessary multiple firings of the enamelled sheets have been carried out.

Recognition was accorded to the novelty of Mr. Knapp's work recently when his methods and some examples of his work were included as part of the B.B.C. television programme "Panorama." In the course of this programme Mr. Knapp demonstrated his methods of preparing the metal surface and of grinding and applying the enamels. The scene then shifted from Mr. Knapp's studio to the works of Stewart and Gray Ltd., where some finished and partly finished pictures were shown entering the furnaces for the fusing operation. Mr. Knapp was interviewed by the B.B.C. commentator Max Robertson, who also introduced an art critic and an architect, both of whom expressed interest in the possibilities of Mr. Knapp's work, which lends itself particularly to application in the form of mural paintings on large, flat panels which can be incorporated into modern architectural schemes.

In the closing sequences of the programme, Mr. N. F. Parker, managing director of Stewart and Gray Ltd., expressed the interest of his company in this new development and their confidence that it would arouse widespread interest.

In the picture above, the artist, Stefan Knapp (right) is seen discussing details of the television presentation of his work with Miss Catherine Dove and Mr. Alexander Moyes of the B.B.C. production unit and with Max Robertson the commentator.

The picture on the left shows a television camera in position in the works of Stewart and Gray Ltd., ready to relay the process of fusing the finished pictures in one of the enamelling furnaces.

TECHNICAL AND INDUSTRIAL APPOINTMENTS

Mr. R. B. Olliver has been appointed director of **Roto-Finish Ltd.**, with special responsibility for development. He is succeeded as sales manager of the Company by Mr. E. B. Christie, while Mr. R. A. Penstone becomes assistant sales manager.

* * *

Mr. L. D. Stewart, overseas relations manager of **Imperial Chemical Industries Ltd., Paints Division,** has been appointed overseas director of the division.

* * *

Dr. J. E. Garside has been appointed Principal of Borough Polytechnic.

* * *

It is announced by **Evans Electroselenium Ltd.**, that Mr. L. T. Jones, 9 Wardlaw Drive, Rutherglen, Glasgow, has been appointed sales and service manager for Scotland.

* * *

Mr. D. H. Haywood, for many years with the Birmingham office of Westinghouse, has been appointed Midland Area manager of **Silvercrown Ltd.** He will have his office at the Birmingham branch of the company, 96 MacDonald Street, Birmingham, 5. Telephone No. Midland 2478.

The Birmingham Depot of the company has been considerably expanded so that most plating and polishing materials are now available from stock and delivered by the company's transport.

ELECTION OF I.V.E. SECTION OFFICERS

The election of officers for the forthcoming 1956-57 Session has been announced by the local sections of the Institute of Vitreous Enamellers as follows:—

Midland Section

Chairman: G. H. Legg.
Vice-Chairman: L. Bayliss.
Hon. Secretary: D. Sleath.
Committee: W. Ball, L. Read and J. A. Clarke.

Southern Section

Chairman: J. J. Guy.
Vice-Chairman: Dr. B. K. Niklewski.
Hon. Secretary: John Hooper.
Committee: A. B. Kent, B.B. Kent, and J. H. Gray.

TRADE and TECHNICAL PUBLICATIONS

"Corrosion and its Prevention at Bimetallic Contacts": This booklet has been published by H.M.S.O. on behalf of the Corrosion and Electrodeposition Committee of the Inter-Service Metallurgical Research Council, price 1s. 6d.

It is an attempt to provide up-to-date and reliable information for the benefit of designers concerned with metallic corrosion.

The text provides general information about the conditions in which bimetallic contacts are most likely to lead to troublesome corrosion and also the means to mitigate these effects, and should be read in conjunction with the Table which follows. By a system of symbols it indicates the relative effects of the corrosion of a range of metals when brought into mutual contact and bridged by water containing an electrolyte. The Table is arranged in two main groups of metals, the first in sequence approximately similar to the "Schedule of Potentials" included in many documents. The second group comprises chromium, stainless steel, titanium and aluminium which develop highly-protective oxide films and behave as relatively noble metals under conditions favourable to the maintenance of such films, but are in some cases less resistant in conditions in which breakdown of the films is possible. It is these metals, in particular, that cause difficulty in attempting to predict the behaviour of bimetallic contacts from a schedule of potentials.

Cellon Bulletin: Vol. 1, No. 2 of this bulletin published by Cellon Ltd., Kingston-on-Thames, Surrey contains a review of the latest developments in paints and protective finishes for all purposes.

Information is given of a new method of spray application known as airless spray. It is claimed to eliminate overspray and its consequent wastage of paint. The method, newly introduced from the United States, does not rely on compressed air for atomization, but instead makes use of a very simple principle. Paint is fed to the gun from a pressure pot in which it is kept at a temperature above the boiling point of its solvents, but under pressure to prevent them from boiling. When paint is released from the gun these solvents suddenly expand and cause atomization. Since the principle involved is essentially that of hot spray application, a heavier film thickness with better flow is claimed to be achieved and a uniform viscosity independent of conditions of temperature or atmosphere can be maintained.

Another feature of the bulletin was the description of British Industries Fair in which the company's products that were on show were described. These included highly resistant stoving and air-drying finishes, tinted etch primers, weldable primer, etc.

"Canning Quarterly News": The April issue of this magazine published by W. Canning and Co Ltd., Birmingham, contains news and information on events that have taken place in the organization.

Included also are details of the company's agents in South Africa and Norway, a report on their technical library, and information on a house-building scheme.

"The Bonderizer": Articles on helicopters, motor cars and motor cycles are included in the April issue of this broadsheet published by The Pyrene Co. Ltd., Metal Finishing Division, Great West Road, Brentford, Middlesex.

The construction of three of the new cars produced by the Ford Motor Co. Ltd., Consul, Zephyr and Zodiac, is described and details are given on the methods by which they are protected against rust and corrosion. The camshafts, tappets and valve stems in the power units are "Parco-Lubrized" before assembly. The largest tipping basket type "Parkerizing" machine in the world for treatment of a multitude of small parts for engines and chassis is at the company's Dagenham works.

Nearby at Briggs Motor Bodies Ltd., the bodies for the new cars are all protected by being conveyed through a complete sequence of cleaning and "Bonderizing" operations in fully automatic "Spra-Bonderizing" plants. The "Bonderite" coating beneath the enamel inhibits rusting and consequent creeping finish failure from an area accidentally damaged by flying stones.

"Jenolite News": This issue, Volume 8, No. 2, is devoted mainly to an article which has been reprinted from the Gas Journal. It deals with the chemical prevention of corrosion, and while the techniques described are intended primarily for the gas industry the fields which they cover are duplicated in many other industries.

It states that corrosion prevention can be achieved effectively only if the steelwork presents a thoroughly clean surface prior to the application of paint or other organic finishes. One of the main problems here is the removal of millscale. After removal of scale and rust, the steelwork is rinsed with water, and after drying or draining, treated with Jenolite "RRN" prior to painting.

Full details of the Jenolite "RRN" process are given and the article also deals with gasholder problems, buried pipelines and cathodic protection.

Latest Developments in PLANT, PROCESSES and EQUIPMENT

Industrial Infra-red Heater

A NEW industrial infra-red heater (Fig. 1) was on show at the Factory Equipment Exhibition. Called the " Radisil," it is being manufactured by the Hanovia Lamps Division of Engelhard Industries Ltd., Slough.

The element consists of a coil of nickel-chrome wire fitted into a silica sheath and is designed to emit infra-red radiation with a peak close to the maximum absorption of water. By enclosing the heated wire it is possible to raise it to a high temperature for a relatively small electrical consumption, while the sheath has a property of directing the radiation at right angles to the axis of the coil, thus avoiding heat losses by axial transmission and scattering.

It is claimed that the sheath offers full protection against splashing and steamy or corrosive atmospheres, and so there is little risk of element failure from this cause, or of contamination of the treated material from scaling.

Model 20 consists of a sheet-steel fabricated housing fitted with mounting brackets and electrical connexion box; a chromium-plated reflector; and an element and removable cadmium-plated safety guard. The complete unit, finished in hammer grey stove enamel, weighs only 4½ lb. and measures 26 in. × 3¾ in. × 3½ in. The element has a rating of 500 or 750 watts.

Models of higher ratings are also in the course of production.

Polythene Tape

A NEW division to market an advanced type of polythene film for packing and protection of goods has been formed by Vitaloid Products (Manchester) Ltd., 11 Duke of York St., St. James's, London, S.W.1.

The name of this material is " Flexothene " and it is claimed to have many advantages over normal polythene film. This material has a guaranteed consistent gauge, is practically non-static and has permanent ink adhesion for excellent colour printing. It is obtainable plain or printed as film, layflat tubing, bags and as laminations with a variety of other packaging materials. An illustrated folder giving full details has just been issued and may be obtained together with samples of all types of Flexothene from the company's Flexothene division at the above address.

Standard Fume Ducts in Plastic

A COMPLETE standard range of polythene and PVC tubes and ducts is now available for the construction of duct lines for corrosive fumes. Fabricated by Rediweld Ltd., 15/17, Cromptôn Way, Crawley, Sussex, the parts are marketed under the trade name Polynert.

The advantage offered by the use of plastics is that they are claimed to be in no way susceptible to corrosion. Another feature of this plastic ducting is that it can be quickly and easily erected by a factory's own maintenance staff, with a further saving in outlay.

Standard sections in the Polynert range are available in 3-ft. lengths, with dimensions graduated in 2-in. steps from 4 to 30 in. The various sections have all the appropriate flanges, elbows, T-pieces, backing rings and joints necessary for fume-disposal systems. The thickness of the sheet stock is 3/16-in. for pipes and fittings, while flanges are based on ¼-in. stock.

To simplify the job of considering the use of Polynert, Rediweld designers have evolved a set of paper cut-outs representing the various standard sections at a scale of 1/12. The designer has merely to lay the cut-outs on the plan view and can observe the results without spending a great deal of time drawing-in the system.

Acid-proof Washers

THE development of a line of rubber lined, acid-proof air washers was recently announced by Automotive Rubber Company, Inc. (ARco), Detroit, U.S.A. Designed for integration into plant ventilation

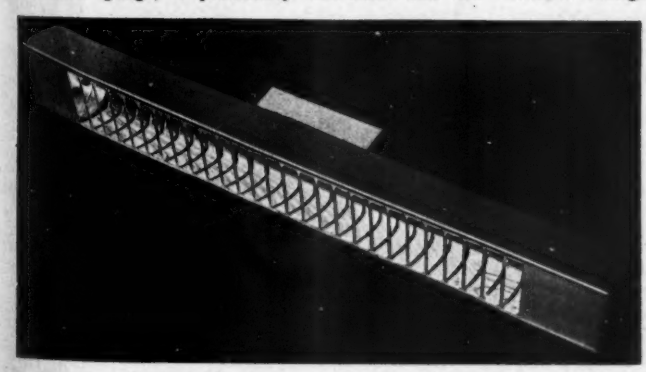


Fig. 1.—Industrial Infra-red Heater

systems, they are said to be capable of eliminating 90 to 99 per cent toxic fumes and corrosives from exhaust gases.

These washers are equipped optionally with straight-through air inlet and discharge; bottom air inlet and top-air discharge; end inlet and end discharge and an added downstream access hatch. Standard units are available in capacities from 7200 to 57600 cu. ft. per min.

The liquid-air contact medium is known as saddle-type tower packing and is claimed to bring the scrubbing liquid and the air, fumes, or other gases into intimate contact within the washer unit.

The essential operating principle is centred in the bed irrigation method. A vertical packing bed is irrigated from the top with a liquid, usually, though not necessarily, water. Liquid is distributed throughout the bed from calibrated drip points producing uniform wetting. This presents a blanket of wet surface area to the passing air or other gas.

The liquid, or water, flows over the surfaces of the packing in thin, low surface-tension films which facilitate penetration of the film surfaces by vapours, fumes, or dust particles in the gas stream. The gas stream is broken up into a multitude of small ribbons, which are forced to follow a roundabout route producing many minute cyclones and whirlpools. This causes sudden changes in the direction of the small gas streams, and starts continual intermingling of the streams as passage is made through the wetted bed.

Construction materials employed in these units in broad variety are available to suit particular service conditions involving high temperatures, oxidizing solutions, fluorine, and HF.

Automatic Degreasing and Drying

A CONVENIENT method of degreasing which has been employed for some considerable time is to use trichlorethylene vapour. This has the advantage of being simple to control, the work is left in a dry condition and a minimum of space is required.

However, degreasing equipment of the open-top manually operated type has two disadvantages:— There is a loss of the toxic trichlorethylene solvent, as a result of draughts and convection; and the efficiency of the process must depend entirely upon the conscientiousness of the operator. Thus there is always the possibility of under-treatment if the component is not held in the solvent vapour for a sufficient time.

The " Perlift " machine has been designed to overcome these disadvantages. It has a totally enclosed construction and an automatic-time cycle, consisting of an evaporating tank, with a thermostatically-controlled electric-heating system, a vapour chamber and an electrically-operated platform hoist. It is available in three standard sizes, and non-standard machines can also be built to order.

The operator places the work on the platform and presses the operating button. The sliding door of the machine is automatically closed, lowering the platform into the vapour chamber, and the component resting on it is degreased by the rising trichlorethylene vapour. When the vapour has risen above the level of the work, a temperature-controlled time mechanism causes the platform to rise through the drying zone into the unload position. At the same time, the sliding door opens and a bell signals the end of the sequence.

The degreasing and drying cycles are independent of the operator. No fumes can escape during the operation, as the sliding door is closed. When the door is opened a suction fan comes into operation to prevent the fumes entering the room.

Perlift machines are manufactured in Switzerland by Technochimie, S.A. Zurich, and are imported by The Electro-Chemical Engineering Co. Ltd., of Weybridge, Surrey.

Welding Gun for Thermoplastics

IT has been announced by Horwitch Smith and Co. Ltd., Pensnett, Staffordshire, that they are the agents in the United Kingdom for the Griesheim electrically and gas-heated TP Welding gun, manufactured by their principals Knapsack-Griesheim A/G, Frankfurt (Main), Germany.

The gun will weld thermoplastics including PVC, polythene, nylon and Perspex. The hot air emerging from the nozzle of the welding gun softens the edges of the material as well as the welding rod. The rod is applied into the seam to be welded by means of a gently applied pressure of the hand. The connexion between the welding rod and the plastic material is achieved by the interlocking of the molecule chains in the heated zones.

A hot-air stream serves as the welding gas, in the case of polythene a hot stream of nitrogen at a temperature of 200 to 400°C. is used. The temperature can be regulated easily and depends upon the type of material being welded.

In the case of the electric gun, a stream of compressed air passes through a hot spiral-heating element, while with the gas gun the gas flame impinges on a heating coil through which the compressed air passes on its way to the welding nozzle.

The welding nozzles are interchangeable and are supplied with diameters of 3, 4 and 5 mm. for the purpose of regulating the hot-air stream to different widths and different speeds.

Rust Proofing Treatment

A NEW de-watering lacquer known as " Water-White " is now being marketed in this country by Tool Treatments (Chemicals) Ltd., Birmingham Row, West Bromwich. This air-drying lacquer can be applied in exactly the same way as ordinary lacquer with the important difference that work to be treated can be dipped wet. This means that products can be transferred from plating, phosphating or other finishing treatment swill tanks to the " Water-White " tank immediately and without the chance of rust forming. The lacquer repels instantly all water and moisture, and provides a thin, tough coating with excellent adhesive properties.

The company state that " Water-White " is the ideal treatment for bright finishes on precision tools and has a wide application in industry generally.

Further information is available from the manufacturers.